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PHOTOCHEMICAL FORMATION OF MONONUCLEAR BIS AND TRIS  
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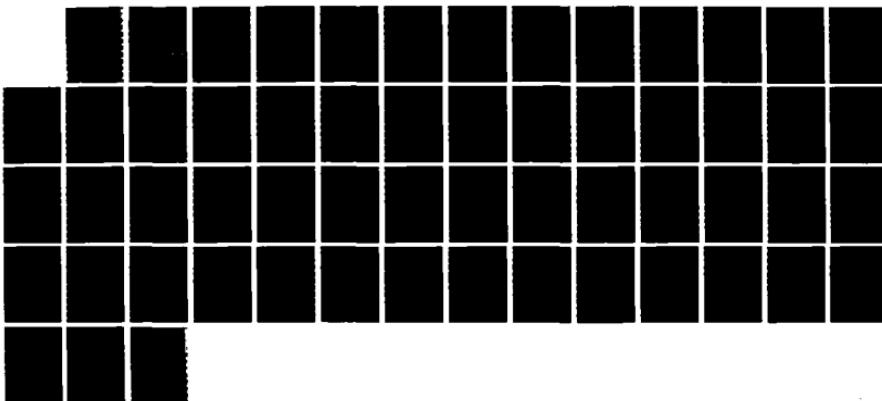
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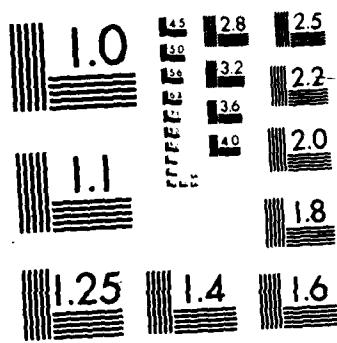
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Photochemical Formation of Mononuclear Bis and Tris Ethylene Complexes  
From Irradiation of Iron Pentacarbonyl or Triruthenium Dodecarcarbonyl:  
Species Involved in Catalytic Alkene Isomerization

by

Yee-Min Wuu, James G. Bentsen, Cynthia G. Brinkley and Mark S. Wrighton

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Abstract

In alkane or  $\text{CF}_3\text{C}_6\text{F}_{11}$  solutions which contain excess  $\text{C}_2\text{H}_4$ , near-UV irradiation of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ , formed quantitatively in situ from visible light ( $\lambda > 420\text{nm}$ ) irradiation of  $\text{Ru}_3(\text{CO})_{12}$ , yields  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  at 298K. At temperatures below 253K further substitution can be effected photochemically to give trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ . Near-UV irradiation of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  in rigid,  $\text{C}_2\text{H}_4$ -saturated, 3-methylpentane glasses at 90K yields  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ , but further CO loss to give cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  is observed after only  $\approx 5\%$  consumption of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ . Isomerization of photogenerated cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  to trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  is only observed on warming the glass above 210K. Prolonged irradiation of photogenerated cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  at 90K yields loss of additional CO to give a monocarbonyl complex, formulated as  $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$ , which reacts on warming with photoreleased CO to initially regenerate cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ . The photochemistry of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  is the same as that of the  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  except that trans- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  could only be detected by IR spectroscopy at temperatures below 210K. The new results show that species previously formulated as  $\text{Fe}_2(\text{CO})_6(\text{alkene})_2$  are in fact  $\text{Fe}(\text{CO})_3(\text{alkene})_2$ . In solution, the  $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  ( $\text{M} = \text{Fe, Ru}$ ) and  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  are substitutionally labile and may serve as versatile reagents in preparative chemistry. Addition of deoxygenated 1-pentene to solutions of the bis and tris  $\text{C}_2\text{H}_4$  complexes results in rapid catalytic isomerization at 293K to a mixture of 2-pentenes, thus establishing the viability of both  $\text{M}(\text{CO})_3$  and  $\text{M}(\text{CO})_2$  species as repeating units in the catalytic alkene isomerization. Deactivation of  $\text{M}(\text{CO})_3(\text{alkene})_2$  as a 1-pentene isomerization catalyst, in the absence of excess CO, proceeds, at least in part, by dehydrogenation of 1-pentene to form the stable, catalytically inactive (at 298K)  $\text{M}(\text{CO})_3(\text{n}^4\text{-1,3-pentadiene})$  complexes.

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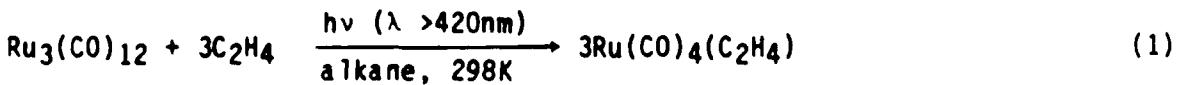
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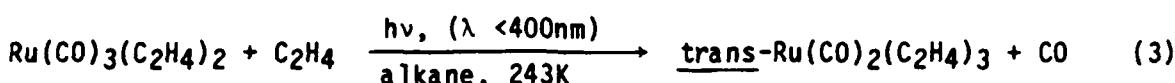
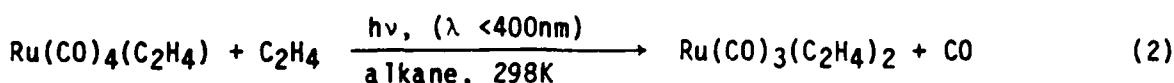
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Research in this group and elsewhere has established that an extraordinarily active alkene isomerization catalyst results from photolysis of  $\text{Fe}(\text{CO})_5$  in the presence of alkenes.<sup>1-3</sup> A carbonyl-bridged diiron complex<sup>4</sup> and, alternatively, a mononuclear tricarbonyl iron unit<sup>1b,3</sup> have been proposed to carry the catalytic cycle. A report from this group<sup>5</sup> establishes that iron carbonyl intermediates in the photocatalytic systems could be observed spectroscopically at sub-ambient temperatures, including  $\text{HFe}(\text{CO})_3(\text{n}^3\text{-C}_3\text{H}_5)$  from photolysis of  $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$  in a rigid alkane glass at 77K. In neat 1-pentene, warmup of photogenerated  $\text{HFe}(\text{CO})_3(\text{n}^3\text{-C}_5\text{H}_9)$  (from  $\text{Fe}(\text{CO})_5/1\text{-pentene}$  at 77K) results in significant catalytic isomerization of 1-pentene above 243K in the dark. Eventual regeneration of  $\text{Fe}(\text{CO})_4(\text{alkene})$  is accompanied by decline of catalytic activity.  $\text{Fe}(\text{CO})_3(\text{n}^3\text{-allyl})$  radical species, also detected at 143K in 1-3% yield as photoproducts of  $\text{Fe}(\text{CO})_5$  and olefins, have been implicated in catalytic reactions of olefins.<sup>6</sup>

New findings reported here reveal the nature of the dominant species resulting from near-UV irradiation of  $\text{Fe}(\text{CO})_5/\text{alkene}$  solutions. Species previously formulated as  $\text{Fe}_2(\text{CO})_6(\text{alkene})_2$ <sup>5</sup> are in fact mononuclear  $\text{Fe}(\text{CO})_3(\text{alkene})_2$  complexes, consistent with a report by Fleckner, Grevels, and Hess.<sup>7</sup> Other important mononuclear Fe species are reported herein including bis and monocarbonyl complexes. We have also extended the low temperature photochemistry to  $\text{Ru}(\text{CO})_4(\text{alkene})$  systems and find that mononuclear bis and tris  $\text{C}_2\text{H}_4$  complexes can be generated photochemically via sequential photochemical reactions represented by equations (1)-(3) for the case of





alkene =  $\text{C}_2\text{H}_4$ . Photochemistry according to equation (1) is known<sup>8-10</sup> and provides an excellent route to  $\text{Ru}(\text{CO})_4$ (alkene) complexes.  $\text{Ru}_3(\text{CO})_{12}$  is a known photocatalyst for alkene reactions such as isomerization<sup>11,12</sup> and hydrosilation;<sup>13</sup> catalytically active mononuclear species have been proposed. Our key finding is that the mononuclear species  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  and  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  can both isomerize 1-pentene in the dark, in accord with the activity found upon photoactivation of  $\text{Ru}_3(\text{CO})_{12}$ .  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  shows very little activity. The results for both the  $\text{Fe}(\text{CO})_5$ /alkene and  $\text{Ru}_3(\text{CO})_{12}$ /alkene systems are consistent with photocatalysis via mononuclear species with no obvious role for cluster complexes. A contributor to deactivation of the catalysts is dehydrogenation of the alkene substrate leading to the formation of inert  $\text{M}(\text{CO})_3(\pi^4\text{-1,3-diene})$  complexes.

Experimental

Materials. The  $\text{Fe}(\text{CO})_5$  and  $\text{Ru}_3(\text{CO})_{12}$  were obtained from Strem Chemicals. The  $\text{Fe}(\text{CO})_5$  was passed through  $\text{Al}_2\text{O}_3$  prior to use and the  $\text{Ru}_3(\text{CO})_{12}$  was used as received. The photochemistry at low temperature was carried out using 3-methylpentane (Aldrich) or methylcyclohexane (J.T. Baker) as the glassing materials. Quantitative  $^1\text{H-NMR}$  data were obtained using  $\text{CF}_3\text{C}_6\text{F}_{11}$  solvent from Fluka AG. The 1-pentene (99% pure) was obtained from Aldrich and passed through  $\text{Al}_2\text{O}_3$  prior to use. Research grade  $\text{CO}$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  were obtained from Matheson. The  $^{13}\text{CO}$  (99%  $^{13}\text{C}$ ) was obtained from Cambridge Isotope Laboratories. The  $\text{PPh}_3$  was recrystallized prior to use.

Instrumentation. IR spectra were recorded using a Perkin Elmer 180 grating instrument or a Nicolet 7199 or 60SX Fourier transform IR spectrometer.  $^1\text{H-NMR}$  spectra were recorded on either a Bruker 270 or 250 MHz Fourier transform instrument using cycloheptane (in the  $\text{CF}_3\text{C}_6\text{F}_{11}$  solvent) as an internal standard, 1.54 ppm vs.  $\text{SiMe}_4$ . The 1-pentene to cis- and trans-2-pentene isomerization was analyzed by gas chromatography using a 30 ft. x 1/8 in. 20% propylene carbonate on chromasorb P column operated at 20°C.

High pressure liquid chromatography (HPLC) was accomplished with a Hewlett-Packard 1084 B chromatograph with a Hewlett-Packard 1040 rapid-scan UV-VIS detector. Detection was made at 254 nm, and separations were accomplished using a LiChrosorb Alox T 5 micron column (250mm x 4.6mm i.d.) with hexane solvent. Identities of molecules associated with the peaks were established by comparison of rapid scan UV-VIS spectra and retention times with those of an authentic sample. Gas chromatograph-mass spectra (GC-MS) were recorded on a Hewlett-Packard model 5992 mass spectrometer. All mass spectra were recorded at 70 ev. Separations were done using a 10 ft. x 1/8 in. SE-30 on chromasorb W column.

Procedures. Generally, all manipulations were carried out under  $N_2$  in a Vacuum Atmospheres dry box or under Ar using conventional Schlenk line techniques. Low temperature irradiations involved the use of a Bausch and Lomb SP200 200W high pressure Hg lamp filtered with a 10 cm Pyrex water filter. Low temperature IR spectra were recorded using a Precision Cell, Inc. Model P/N 21.000 variable temperature cell or CTI-Cryogenics Model 21 cryocooler equipped with  $CaF_2$  windows. Sample temperatures are estimated to be  $\pm 2K$  at a fixed temperature.

Clean solutions of  $Fe(CO)_4(C_2H_4)$  were prepared by near-UV photolysis of  $4 \times 10^{-3}$  M  $Fe(CO)_5$  at 273K in  $C_2H_4$ -saturated alkane solution until no  $Fe(CO)_5$  remained by IR. At this point, both  $Fe(CO)_4(C_2H_4)$  and  $Fe(CO)_3(C_2H_4)_2$  were present. The mixture was then purged with CO and warmed to 298K to yield  $Fe(CO)_4(C_2H_4)$  as the only detectable metal carbonyl. Clean solutions of  $Fe(CO)_3(C_2H_4)_2$  were obtained by continuing to photolyze the  $C_2H_4$ -saturated solution at <273K until no  $Fe(CO)_4(C_2H_4)$  remained, as established by IR. The  $Ru(CO)_4(C_2H_4)$  was prepared quantitatively via visible light ( $\lambda > 420$  nm) irradiation of  $\sim 1 \times 10^{-3}$  M  $Ru_3(CO)_{12}$  in a continuously  $C_2H_4$ -purged alkane solution using a filtered Hanovia 450W medium pressure Hg lamp. The  $Ru(CO)_3(C_2H_4)_2$  solutions were prepared by subsequent near-UV irradiation of a  $Ru(CO)_4(C_2H_4)$  solution at 298K in the presence of  $C_2H_4$ . Only  $Ru(CO)_4(C_2H_4)$  and  $Ru(CO)_3(C_2H_4)_2$  were spectroscopically detected in these solutions. After  $\sim 90\%$  conversion of  $Ru(CO)_4(C_2H_4)$ , the photolysis was stopped and the solution was purged with  $C_2H_4$  to remove photogenerated CO. The trans- $Ru(CO)_2(C_2H_4)_3$  solutions were prepared by irradiation at 232K (liquid  $N_2/CH_3CN$  bath) of an alkane solution containing  $Ru(CO)_3(C_2H_4)_2$  and  $Ru(CO)_4(C_2H_4)$  under a slow purge of  $C_2H_4$  necessary to remove photogenerated CO. Only  $Ru(CO)_3(C_2H_4)_2$  and trans- $Ru(CO)_2(C_2H_4)_3$  were detectable by IR in these solutions. In order to

avoid secondary photodecomposition the irradiations were discontinued after approximately 70% conversion to trans-Ru(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>.

Photolysis of M(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) (M = Fe, Ru), in a C<sub>2</sub>H<sub>4</sub>-saturated CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub> solution, was monitored by <sup>1</sup>H-NMR by first generating the M(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) in situ in a septum-sealed NMR tube containing the cycloheptane internal standard. The NMR of the sample was then recorded at the temperature of the subsequent irradiation. Irradiations were carried out in a clear Dewar flask at the temperature necessary to observe the M(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (Fe, 273K; Ru, 298K) or trans-Ru(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> (243K). IR spectral changes for the Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) to Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> conversion showed the same extent conversion as determined by <sup>1</sup>H-NMR for the same solution, thereby establishing correlation of IR absorptions and the <sup>1</sup>H-NMR singlet attributed to Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>.

The 1-pentene isomerization kinetics were determined by generating a methylcyclohexane solution of the appropriate catalyst precursor and removing excess C<sub>2</sub>H<sub>4</sub>, which inhibits the isomerization, by a vigorous Ar purge at 195K, a temperature at which the M(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (M = Fe, Ru) and Ru(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> are stable in the absence of C<sub>2</sub>H<sub>4</sub>. The appropriate amount of pre-cooled 1-pentene, passed through Al<sub>2</sub>O<sub>3</sub> and deoxygenated by three freeze-pump-thaw cycles, was added at 195K, a temperature where no catalytic isomerization occurs. Rapid warming to 273K initiated catalysis. A syringe was used to withdraw samples from the solution for analysis. Instantaneous deactivation of the catalyst was achieved by mixing the drawn aliquot with a saturated solution of PPh<sub>3</sub> in methylcyclohexane. The volatiles were stripped off under vacuum and condensed in liquid N<sub>2</sub> cooled traps. The condensate, containing a mixture of the linear pentenes, was subsequently analyzed by gas chromatography.

Fe(CO)<sub>2</sub>(<sup>13</sup>CO)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> was prepared in situ by reacting Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> with 1 atm of <sup>13</sup>CO in methylcyclohexane or 3-methylpentane at 298K to form

$\text{Fe}(\text{CO})_3(^{13}\text{CO})(\text{C}_2\text{H}_4)$ . Excess  $^{13}\text{CO}$  was purged from the solution by  $\text{C}_2\text{H}_4$  at 298K and the resulting  $\text{C}_2\text{H}_4$ -saturated solution was irradiated at 273K to convert  $\text{Fe}(\text{CO})_3(^{13}\text{CO})(\text{C}_2\text{H}_4)$  to  $\text{Fe}(\text{CO})_{3-n}(^{13}\text{CO})_n(\text{C}_2\text{H}_4)_2$  ( $n = 0, 1$ ). The  $\text{Fe}(\text{CO})_{5-n}(^{13}\text{CO})_n$  was prepared by  $\lambda > 540$  nm irradiation of  $\text{Fe}_3(\text{CO})_{12}$  in a  $^{13}\text{CO}$ -saturated 3-methylpentane solution at 298K.

Results and Discussion

a. Mononuclear Ru Carbonyl-Ethylene Complexes. UV-VIS, IR and  $^1\text{H-NMR}$  spectral data for relevant complexes are reported in Tables I, II, and III respectively. Irradiation of  $\text{Ru}_3(\text{CO})_{12}$  in  $\text{C}_2\text{H}_4$ -saturated alkane (3-methylpentane or methylcyclohexane) or  $\text{CF}_3\text{C}_6\text{F}_{11}$  solutions yields  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ , equation (1), as expected. Indeed, for excitation using wavelengths of light longer than  $\sim 420$  nm, where  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  does not absorb significantly, the generation of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  is quantitative. Thus, visible irradiation of  $\text{Ru}_3(\text{CO})_{12}$  in the presence of  $\text{C}_2\text{H}_4$  provides an excellent route to  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ . If  $\text{C}_2\text{H}_4$  is purged from solution by Ar at 298K,  $\text{Ru}_3(\text{CO})_{12}$  is regenerated quantitatively.

Near-UV irradiation of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  in the presence of  $\text{C}_2\text{H}_4$  leads to additional spectral (IR and NMR) changes that are consistent with the photosubstitution represented by equation (2), Figures 1 and 2 and Table IV. In particular, in the  $^1\text{H-NMR}$ , Figure 1, we observe that the singlet at 2.10 ppm due to  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  declines and a new singlet at 2.50 ppm grows. Quantitative analysis from several NMR-monitored photoreactions, Table IV, indicates that the photoproduct has a 1:2 ratio of Ru: $\text{C}_2\text{H}_4$ . The IR spectral changes that occur at 298K are essentially duplicated when the  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  is irradiated in a rigid  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane glass at 90K. The initial ( $\sim 5\%$  conversion) IR spectral changes for the 90K photolysis reveal the generation of free CO ( $2132\text{ cm}^{-1}$ )<sup>14</sup> in the glass and growth of the characteristic  $2082\text{ cm}^{-1}$  feature ( $2081\text{ cm}^{-1}$  in solution at 298K) of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . The rigid glass precludes the rapid diffusion of a presumed  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$  intermediate, thus ruling out polynuclear species, and in particular  $\text{Ru}_2(\text{CO})_6(\text{C}_2\text{H}_4)_2$ , as photoproducts. However, the low molecular weight of  $\text{C}_2\text{H}_4$  and its high concentration,  $\sim 0.05\text{ M}$ ,<sup>15</sup> allows reaction of the photogenerated  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$  (not observed at 90K) with  $\text{C}_2\text{H}_4$  to form  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . The  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  is very photosensitive and,

after ~5% conversion of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  at 90K, there is evidence for secondary product formation (vide infra) by further loss of CO from the  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . Such is not the case at 298K in fluid solutions, where extensive accumulation of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  is achieved. Accumulation of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  is probably a result of rapid back reaction of secondary photoproducts, such as  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  (vide infra), with liberated CO.

At 90K, in either 3-methylpentane or the more rigid methylcyclohexane, irradiation of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  is only observed to give  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ , presumably because excess  $\text{C}_2\text{H}_4$  present in the glass reacts with the 16-electron  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$  fragment. By irradiating  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  in a 3-methylpentane glass at 55K a new species assigned as the  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$  fragment can be detected. The IR spectral band pattern for  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$  (2055, 1978, 1972  $\text{cm}^{-1}$ ; 3-methylpentane, 55K) is similar to that for  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ ,<sup>5</sup> Table II. The ability to detect the  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$  at the lower temperature reflects slower  $\text{C}_2\text{H}_4$  diffusion and/or a slower rate of  $\text{C}_2\text{H}_4$  binding to the unsaturated Ru center. Warmup to 90K of the irradiated 55K glass results in rapid conversion of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$  to  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ .

For  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ , the IR spectrum in the CO stretching region is consistent with a  $\text{C}_{2v}$  local symmetry of the  $\text{Ru}(\text{CO})_3$  fragment [ $\nu(\text{CO}) = 2081$  (w,  $\text{A}_1$ ), 2005 (m,  $\text{A}_1$ ) and 1995  $\text{cm}^{-1}$  (s,  $\text{B}_1$ ); 3-methylpentane, 298K] possible when the alkene ligands lie in the equatorial plane of a trigonal bipyramidal structure, as predicted by theory for  $\text{Fe}^{16}$  complexes and established for the spectroscopically similar and structurally characterized  $\text{Ru}(\text{CO})_3(\eta^2\text{-methylacrylate})_2$ ,<sup>9</sup>  $\text{Fe}(\text{CO})_3(\eta^2, \eta^2\text{-1,5-dimethylene-2,6-dimethylcyclooctane})$ <sup>17</sup> and  $\text{Fe}(\text{CO})_3(\eta^2\text{-trans-cyclooctene})_2$ <sup>7</sup> complexes. The singlet in the  $^1\text{H-NMR}$  for  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  is consistent with such a coordination geometry or with a dynamic geometry at temperatures as low as 243K.

Near-UV irradiation of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in low temperature fluid  $\text{CF}_3\text{C}_6\text{F}_{11}$  (243K) or alkane (233K) solutions saturated with  $\text{C}_2\text{H}_4$  leads to additional spectral changes (NMR and IR) that are consistent with the photosubstitution represented in equation (3), Figures 3 and 4 and Table V. The  $^1\text{H-NMR}$ , Figure 3, shows that a singlet at 3.02 ppm grows at the expense of singlets attributed to  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  and its precursor  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ . Quantitative analysis of the  $^1\text{H-NMR}$  spectral changes for several experiments, Table V, shows the  $\text{Ru:C}_2\text{H}_4$  ratio to be 1:3 for the 3.02 ppm feature. A corresponding single product absorption at  $1956\text{ cm}^{-1}$  in the CO stretching region of the IR, Figure 4, is consistent with a cylindrical local symmetry of a  $\text{Ru}(\text{CO})_2$  fragment and, consequently, formulation of the product as trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  having three equatorially disposed  $\text{C}_2\text{H}_4$  ligands in a trigonal bipyramidal structure. To our knowledge, this represents the first reported preparation of an  $\text{M}(\text{CO})_2(\text{alkene})_3$  ( $\text{M} = \text{Fe, Ru, Os}$ ) complex.

Surprisingly, trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ , observed as a photoproduct in low temperature fluid solutions, is not observed as a product in the near-UV photolysis of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in a  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane glass at 90K. However, CO loss from  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  does occur in low temperature organic glasses. We have exploited the properties of methylcyclohexane to establish the photochemical properties of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . It must be pointed out that the investigation of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  involves solutions which invariably contain excess  $\text{C}_2\text{H}_4$  in order to preserve purity of the  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  while manipulating the samples prior to cooling them to the low temperature of the rigid glasses. Unlike 3-methylpentane, a methylcyclohexane glass at 90K inhibits the reaction of excess  $\text{C}_2\text{H}_4$ ,  $\text{N}_2$ , or CO with a number of well established 16-electron photoproduct species. However, warming of such a glass to  $\sim 110\text{K}$  retains its integrity while greatly accelerating bimolecular reactions of stationary

16-electron intermediates with diffusing small ligands to form characterized 18-electron substitution complexes.<sup>18</sup> Near-UV irradiation of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in a methylcyclohexane glass containing excess  $\text{C}_2\text{H}_4$  at 90K results in the IR spectral changes shown in Figure 5. A feature attributed to photoejected CO ( $2132 \text{ cm}^{-1}$ ) and two bands attributed to the 16-electron  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$  species at 2020 and  $1948 \text{ cm}^{-1}$  grow while features attributed to  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  decline. Warming the matrix to 110K results in complete loss of  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$  absorptions, but there is growth of carbonyl absorptions at 2019 and  $1975 \text{ cm}^{-1}$  which remain upon recooling to 90K. Importantly, the amount of photoejected CO ( $2132 \text{ cm}^{-1}$ ) in the glass remains constant during annealing to 110K (see insets; Figure 5a and b), ruling out formation of another isomer of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  by reaction of CO with  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ . The IR shows that trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  ( $\nu(\text{CO}) = 1953 \text{ cm}^{-1}$ ) is not formed in detectable amounts. The spectral features obtained are those observed for the 90K photolysis of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane. These results imply the formation of an 18-electron  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  species which we formulate as cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ , containing one equatorial and one axial CO ligand in a trigonal bipyramidal structure. In support of this formulation, a OC-Ru-CO bond angle of  $81^\circ$  is calculated for the  $\text{Ru}(\text{CO})_2$  fragment by evaluation<sup>19</sup> of the ratio of the relative intensities of the symmetric and antisymmetric carbonyl absorbances. Furthermore, warmup of cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  to 210K leads to net IR spectral changes which are retained on recooling to 90K, consistent with quantitative conversion to the trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  complex ( $1953 \text{ cm}^{-1}$ ) mentioned above. In  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane glasses at 90K, photochemical isomerization of matrix isolated trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  to the cis-form is accompanied by loss of CO to form a monocarbonyl species ( $1964 \text{ cm}^{-1}$ ), presumably a  $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$  complex, related to well-characterized  $\text{Fe}(\text{CO})(\text{diene})_2$  complexes.<sup>20</sup>

$\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$  can also be obtained directly by photolysis of cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  at 90K in  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane. Warmup of 90K glasses containing the  $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$  and the photogenerated CO results, initially, in formation of cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ , and, eventually, trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  at higher temperatures. In methylcyclohexane the photoconversion of cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  to  $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$  ( $1964 \text{ cm}^{-1}$ ) proceeds via transient formation of a second monocarbonyl species ( $1923 \text{ cm}^{-1}$ ) tentatively formulated as the coordinatively unsaturated  $\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_3$ . At high  $\text{C}_2\text{H}_4$  concentrations in the dark at 90K, the  $1964 \text{ cm}^{-1}$  feature grows in at the expense of the photogenerated  $1923 \text{ cm}^{-1}$  feature without change in the amount of free CO ( $2132 \text{ cm}^{-1}$ ) detected in the glass.

The thermally labile  $\text{Ru}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$  ( $n = 4, 3$ ) complexes are stabilized by excess  $\text{C}_2\text{H}_4$  toward decomposition in fluid solutions at 298K, but are quite stable in Ar-purged alkane solutions at sufficiently low temperatures (195K). The trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  is more labile than the bis- $\text{C}_2\text{H}_4$  complex and back reacts with photoreleased CO at  $\sim 253\text{K}$  to regenerate  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . Purging a  $\text{C}_2\text{H}_4$ -saturated alkane solution of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  with Ar at 298K rapidly generates  $\text{Ru}_3(\text{CO})_{12}$ ; purging with CO at 298K yields  $\text{Ru}(\text{CO})_5$ ; and reaction with 0.05 M  $\text{PPh}_3$  at 298K yields  $\text{Ru}(\text{CO})_4\text{PPh}_3$ . The  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  reacts with CO to yield first  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ , then  $\text{Ru}(\text{CO})_5$ ; reaction with 0.05 M  $\text{PPh}_3$  yields  $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ ; and reaction with trans-1,3-pentadiene rapidly yields  $\text{Ru}(\text{CO})_3(\text{trans-1,3-pentadiene})$ .

b. Mononuclear Fe Carbonyl-Ethylene Complexes. The formation of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  from  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ , and work published by Fleckner, Grevels, and Hess<sup>7</sup> prompted us to reinvestigate the alkene products derived from the low temperature photolysis of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ . Irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  at 273K in the presence of  $\text{C}_2\text{H}_4$  results in the formation of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ , not  $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{H}_4)_2$  as previously concluded.<sup>5</sup> The  $^1\text{H-NMR}$  and IR spectral changes accompanying

photolysis of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  in  $\text{C}_2\text{H}_4$ -saturated  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution are shown in Figures 6 and 7, respectively. The  $^1\text{H-NMR}$  integrations show that the product associated with the singlet at 2.68 ppm has two  $\text{C}_2\text{H}_4$  ligands per Fe, not one  $\text{C}_2\text{H}_4$  as concluded previously, consistent with conversion of 1.05  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  and 1.00  $\text{C}_2\text{H}_4$  to 0.98  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . In the earlier work,<sup>5</sup>  $^1\text{H-NMR}$  integration data were unreliable, presumably owing to sample decomposition. In the present work IR spectral changes for the same solution show the same extent conversion as determined by  $^1\text{H-NMR}$ , thereby establishing correlation of IR absorptions and the  $^1\text{H-NMR}$  singlet attributed to  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . The remarkable spectroscopic similarity to  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  suggests the same  $\text{C}_{2v}$  structure for both the Fe and Ru species.

Irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  in a  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane glass at low temperature results in the ultimate formation of a monocarbonyl Fe complex, possibly  $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$ , not trans- $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  as previously concluded.<sup>5</sup> As with  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ , loss of CO ( $2132 \text{ cm}^{-1}$ ) from  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  initially yields  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  (Figure 7b); here competitive loss of  $\text{C}_2\text{H}_4$  leads to formation of some  $\text{Fe}(\text{CO})_4$  ( $1946 \text{ cm}^{-1}$ ). [The  $\text{Fe}(\text{CO})_4$  can be photogenerated independently by irradiation of  $\text{Fe}(\text{CO})_5$  under the same conditions.] However, just beyond the initial stages of reaction we find that further photoreaction of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  occurs to yield new carbonyl features at  $1955$  and  $1998 \text{ cm}^{-1}$  which are only detected by spectral subtraction of masking absorptions of unreacted  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ . The  $1955$  and  $1998 \text{ cm}^{-1}$  features are associated with cis- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  (vide infra). This secondary photoproduct is also photosensitive and continued irradiation, Figure 7c (320 sec  $\text{h}\nu$ ), yields only a single carbonyl product band at  $1952 \text{ cm}^{-1}$ . The total yield of liberated CO ( $2132 \text{ cm}^{-1}$ ) per  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  molecule consumed is three times that observed in the initial photoconversion (4 sec  $\text{h}\nu$ ) to  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . The

cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> escaped detection in previous work,<sup>5</sup> presumably as a result of spectral masking by unreacted Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) and the 1952 cm<sup>-1</sup> product band.

As for Ru(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>, photolysis at 100K of a C<sub>2</sub>H<sub>4</sub>-saturated 3-methylpentane glass containing only Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> proceeds cleanly at low extent conversion to give well resolved spectral features associated with cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>, 1955 and 1998 cm<sup>-1</sup> with a calculated OC-M-CO angle of 82°, Figure 8. Our new data show that trans-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> is not observed in C<sub>2</sub>H<sub>4</sub>-saturated alkane glasses as a product of 100K photolysis of Fe(CO)<sub>n</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>5-n</sub> (n = 5, 4, 3). However, warmup of photogenerated cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> to 200K, Figure 8b, results in decline of its spectral features, significant regeneration of Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>, and growth of a single band at 1942 cm<sup>-1</sup> which remains upon recooling to 100K. We attribute this band to trans-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>, in analogy with the <sup>1</sup>H-NMR characterized trans-Ru(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>. The trans-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> back reacts with the free CO upon warming above 210K. The trans-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> cannot be detected by <sup>1</sup>H-NMR upon photolysis of Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> in C<sub>2</sub>H<sub>4</sub>-saturated CF<sub>3</sub>C<sub>6</sub>F<sub>11</sub> solutions at temperatures as low as 243K, presumably because back reaction of the tris-C<sub>2</sub>H<sub>4</sub> complex with CO occurs rapidly. Photolysis of photogenerated cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> at 90K in the presence of C<sub>2</sub>H<sub>4</sub> generates only the 1952 cm<sup>-1</sup> feature and free CO (2132 cm<sup>-1</sup>). Here, the final yield of liberated CO per Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> molecule consumed is two times that observed in the initial conversion to cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>. Warmup to 150K of alkane glasses exhibiting only the 1952 cm<sup>-1</sup> band and liberated CO results in regeneration of only cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> in high yield with respect to the known concentration of starting material, be it Fe(CO)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>) or Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>. The cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> spectral features are retained upon recooling to 90K, and subsequent near-UV irradiation results in liberation of free CO and regeneration of the 1952 cm<sup>-1</sup> feature at the expense of cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> features. The new data show that both Fe(CO)<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> and cis-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> are extremely photosensitive

and simply do not accumulate during irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  in  $\text{C}_2\text{H}_4$ -saturated alkane glasses. The  $1952 \text{ cm}^{-1}$  feature was previously attributed<sup>5,21</sup> to  $\text{trans-Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ . However, this new set of experiments suggests that the  $1952 \text{ cm}^{-1}$  band is associated with a metal-alkene complex retaining only one CO, namely  $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$ .  $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$  is relatively photoinert and is unchanged after 1 h of irradiation at 100K where  $\sim 15$  min is required to convert  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  to the  $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$ .

Isotopic labelling experiments further support the IR spectral assignments for  $\text{Fe}(\text{CO})_{5-n}(\text{C}_2\text{H}_4)_n$  complexes.  $\text{Fe}(\text{CO})_3(^{13}\text{CO})(\text{C}_2\text{H}_4)$  is prepared by reacting  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  with  $^{13}\text{CO}$  in 3-methylpentane at 298K. Subsequent near-UV irradiation in a  $\text{C}_2\text{H}_4$ -saturated solution at 273K yields  $\text{Fe}(\text{CO})_{3-n}(^{13}\text{CO})_n(\text{C}_2\text{H}_4)_2$  ( $n = 0, 1$ , vide infra). After cooling the solution of  $\text{Fe}(\text{CO})_{3-n}(^{13}\text{CO})_n(\text{C}_2\text{H}_4)_2$  to 90K, extended near-UV irradiation yields species formulated as  $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$  ( $1952 \text{ cm}^{-1}$ ) and  $\text{Fe}(^{13}\text{CO})(\text{C}_2\text{H}_4)_4$  ( $1908 \text{ cm}^{-1}$ ) in a 3:1 ratio, assuming the absorptivities of the  $^{12}\text{CO}$  and  $^{13}\text{CO}$  species to be the same. The absence of observable vibrational coupling is consistent with a monocarbonyl formulation. Warmup to 150K yields cis- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  ( $1998, 1955 \text{ cm}^{-1}$ ; 3-methylpentane, 90K) and cis- $\text{Fe}(\text{CO})(^{13}\text{CO})(\text{C}_2\text{H}_4)_3$  ( $1984, 1924 \text{ cm}^{-1}$ ; 3-methylpentane, 90K) as the only products, which persist on recooling to 90K. The CO stretching ( $K$ ) and interaction ( $K_f$ ) force constants have been calculated for the  $\text{C}_{2v}$   $\text{Fe}(\text{CO})_2$  fragment of cis- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  by normal coordinate analysis<sup>22</sup> ( $K = 1578.3$ ,  $K_f = 34.3 \text{ Nm}^{-1}$ ) and used to correctly predict ( $1985.0, 1923.8 \text{ cm}^{-1}$ ) the observed frequencies for cis- $\text{Fe}(\text{CO})(^{13}\text{CO})(\text{C}_2\text{H}_4)_3$ . Warmup of cis-tris- $\text{C}_2\text{H}_4$  complex to 200K yields trans- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  ( $1945 \text{ cm}^{-1}$ ) and trans- $\text{Fe}(\text{CO})(^{13}\text{CO})(\text{C}_2\text{H}_4)_3$  ( $1918 \text{ cm}^{-1}$ ). The small wavenumber shift between these two features ( $\Delta\nu = 27 \text{ cm}^{-1}$ ) rules out formulation as a monocarbonyl species and suggests a strong interaction force constant for the cylindrical  $\text{Fe}(\text{CO})_2$  fragment of trans- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  ( $K = 1570.4$ ,

$K_f = 39.8 \text{ Nm}^{-1}$ ). At low temperature, the monocarbonyl photoproduct distribution and the absence of cis- or trans- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  during subsequent warmup (1) rules out rapid disproportionation of  $\text{Fe}(\text{CO})_2(\text{CO})_2(\text{C}_2\text{H}_4)_2$  or  $\text{Fe}(\text{CO})_3(\text{CO})(\text{C}_2\text{H}_4)$  at  $< 273\text{K}$  or  $< 298\text{K}$ , respectively, or thermal substitution of  $^{12}\text{CO}$  by excess  $^{13}\text{CO}$  on  $\text{Fe}(\text{CO})_3(\text{CO})(\text{C}_2\text{H}_4)$  at  $< 298\text{K}$  and (2) suggests predominant recombination of the matrix isolated monocarbonyl with CO initially photoejected from the same metal center to form cis-, then trans- $\text{Fe}(\text{CO})_{2-n}(\text{CO})_n(\text{C}_2\text{H}_4)_3$  ( $n = 0, 1$ ) during warmup from 90K to 200K.

The conspicuous absence of trans- $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  species ( $\text{M} = \text{Fe, Ru}$ ) as initial photoproducts from  $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in alkane glasses has been investigated further. In a methylcyclohexane glass, FTIR spectral features attributed to the 16-electron  $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ , (2003 1938  $\text{cm}^{-1}$ ; methylcyclohexane, 100K) and free CO are generated upon photolysis of matrix isolated  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ , Figure 9, in analogy with data for the Ru analog. However, the growth of additional features at 2041(m), 1963(m) and 1957(s)  $\text{cm}^{-1}$  in constant ratio with these is attributed to the concomitant generation of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ , Table II, which has been characterized previously in alkane<sup>5</sup> and Ar<sup>23</sup> matrices as the product obtained upon light-induced loss of CO from  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ . Competitive loss of CO and olefin has previously been observed for  $\text{Fe}(\text{CO})_3(\eta^4\text{-1,3-diene})$  species.<sup>23</sup> We cannot rule out a similar competition for  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ , since we are unable to remove excess  $\text{C}_2\text{H}_4$  which might scavenge  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$ , if it formed.  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$  exhibits a weak electronic absorption at 447 nm, consistent with a coordinatively unsaturated product, Table I. In the presence of excess  $\text{C}_2\text{H}_4$ , warmup of a 90K glass containing  $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_2$  and  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$  to 110K yields net FTIR spectral changes which persist on recooling to 90K. These spectral changes are consistent with conversion of  $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_2$  to cis- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  (as observed for Ru), and also regeneration of the  $\text{C}_{2v}$  symmetry isomer of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  as a result of thermal back reaction

of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$  with  $\text{C}_2\text{H}_4$ . These results are consistent with the net conversion of  $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  to cis- $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  via the 16-electron  $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_2$  intermediate and the net conversion of  $\text{M}(\text{CO})_4(\text{C}_2\text{H}_4)$  to the  $\text{C}_{2v}$  isomer of  $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  via the 16-electron  $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)$  intermediate in  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane. The metal carbonyl features for the 16-electron  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$  show similarities in relative energy and intensity to those of the  $\text{C}_{2v}$   $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ , Table II, thereby suggesting little rearrangement of the  $\text{Fe}(\text{CO})_3$  unit of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$  on reaction with  $\text{C}_2\text{H}_4$ . Also, OC-M-CO<sup>19</sup> bond angles of 97° (M = Ru) and 94° (M = Fe) are calculated for 16-electron  $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_2$  complexes. A cis- geometry for the  $\text{M}(\text{CO})_2$  fragment of the coordinatively unsaturated  $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_2$  intermediate is apparently retained upon reaction with  $\text{C}_2\text{H}_4$ , explaining the conspicuous absence of the thermodynamically favored trans- $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  complexes in the low temperature photolysis of matrix isolated  $\text{M}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  (M = Ru, Fe) to yield cis- $\text{M}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ .

Like  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ ,  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  is very labile at 298K. However,  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  is less labile than  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ . For example, purging an alkane solution of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  with CO yields a pure solution of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$ , a substance that is difficult to obtain in a pure state by conventional procedures. As noted above, CO reacts rapidly with  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  to yield  $\text{Ru}(\text{CO})_5$  under conditions where  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  is inert. Further, the reaction of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  with 0.05 M  $\text{PPh}_3$  at room temperature yields  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)(\text{PPh}_3)$ , with only minor amounts of  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ , whereas  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  gives exclusively  $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ . Reaction of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  with trans-1,3- or 1,4-pentadiene yields  $\text{Fe}(\text{CO})_3(\text{trans}-1,3\text{-pentadiene})$  in analogy to the Ru species. The simple generation of pure alkane solutions of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  allows this complex to serve as an excellent, versatile  $\text{Fe}(\text{CO})_3$  transfer reagent promising a wide range of applications including its use in mechanistic studies of the  $\text{Fe}(\text{CO})_5$  photocatalyzed reactions of alkenes.

c. Catalytic Isomerization of 1-Pentene.  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  readily undergoes alkene exchange as detected by IR spectroscopy. Addition of precooled 1-pentene to an Ar-purged methylcyclohexane (no excess  $\text{C}_2\text{H}_4$  present) solution containing  $\sim 1 \text{ mM}$   $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  at 195K, followed by warming to 260K, results in the decline of spectral features for  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  and growth of new features attributed to  $\text{Ru}(\text{CO})_3(\text{pentene})_2$ , Table II. This assignment is based on the spectral similarity to the bis- $\text{C}_2\text{H}_4$  complex and the shift to lower frequencies consistent with the substitution of  $\text{C}_2\text{H}_4$  by 1-pentene [cf. the IR data of the corresponding  $\text{Fe}(\text{CO})_4(\text{n}^2\text{-alkene})$  complexes]. Continued warming leaves the IR spectral features initially unchanged at 293K. However, gas chromatographic analysis of the solution shows that 1-pentene undergoes catalytic isomerization above 260K, yielding cis- and trans-2-pentene. Turnover numbers exceeding 250 have been obtained in the dark. The trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  is more labile than  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  and undergoes substitution by added 1-pentene at 240K to form trans- $\text{Ru}(\text{CO})_2(\text{pentene})_3$ , Table II. Interestingly, catalytic activity is displayed by trans- $\text{Ru}(\text{CO})_2(\text{alkene})_3$  above 240K with turnover numbers near 50. Some representative data for catalytic 1-pentene isomerization are given in Table VI. Turnover rates, Table VI, decrease systematically with reaction time at 293K in correlation with declining  $\text{Ru}(\text{CO})_3(\text{pentene})_2$  or  $\text{Ru}(\text{CO})_2(\text{pentene})_3$  spectral features. The range of catalyst concentrations used is limited to  $< 6 \text{ mM}$  by solubility of the  $\text{Ru}_3(\text{CO})_{12}$  precursor and to  $> 1 \text{ mM}$  by low turnover numbers. With these restrictions we note that for two different catalyst concentrations within this range the average turnover rates after similar reaction times are in close agreement, suggesting kinetics first-order in metal concentration for both the  $\text{Ru}(\text{CO})_3(\text{alkene})_2$  and trans- $\text{Ru}(\text{CO})_2(\text{alkene})_3$  complexes, in accord with the more detailed report<sup>7</sup> for  $\text{Fe}(\text{CO})_3(\text{pentene})_2$ . Importantly, the initial (1 minute) average turnover rate achieved with trans- $\text{Ru}(\text{CO})_2(\text{pentene})_3$  ( $> 9 \text{ min}^{-1}$ ) at 293K represents a lower limit due to rapid catalyst deactivation, and it clearly exceeds the rate achieved with

$\text{Ru}(\text{CO})_3(\text{pentene})_2$  ( $\sim 4 \text{ min}^{-1}$ ) under the same conditions ( $[\text{catalyst}] = 2.78 \text{ mM}$ ,  $[\text{pentene}] = 1.83 \text{ M}$ , 293K, methylcyclohexane). Under photocatalytic conditions, efficient photochemical conversion of  $\text{Ru}(\text{CO})_3(\text{pentene})_2$  to trans- $\text{Ru}(\text{CO})_2(\text{pentene})_3$  is offset by facile thermal back reaction unless liberated CO is deliberately removed. The importance of  $\text{M}(\text{CO})_2(\text{pentene})_3$  species ( $\text{M} = \text{Fe, Ru}$ ) under photocatalysis conditions is therefore ambiguous. Our results suggest that substitutionally labile  $\text{Ru}(\text{CO})_3(\text{alkene})_2$  and  $\text{Ru}(\text{CO})_2(\text{alkene})_3$  complexes play key roles in the  $\text{Ru}_3(\text{CO})_{12}$  photocatalyzed alkene isomerization, since we have demonstrated that their photogeneration from  $\text{Ru}_3(\text{CO})_{12}$  provides an entrance to the catalytic cycle, Table VI.11. With  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  we have been able to achieve turnover numbers in the dark approaching 2000, and turnover rates of  $\sim 600 \text{ min}^{-1}$  at 293K. These results are in qualitative agreement with the report by Grevels and coworkers<sup>7</sup> in which  $\text{Fe}(\text{CO})_3(\text{n}^2\text{-cis-cyclooctene})_2$  was used as a catalyst precursor. Although solutions of  $\text{Fe}(\text{CO})_3(\text{alkene})_2$  containing 1-pentene approach the equilibrium of the three pentene isomers rapidly and in constant thermodynamic ratio<sup>24</sup> (trans/cis-2-pentene = 3.8), the same cannot be said for the Ru catalysts. An initial ratio of  $\sim 6$  for trans/cis-2-pentene is achieved photochemically using  $\text{Ru}_3(\text{CO})_{12}$  or thermally using  $\text{Ru}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$  ( $n = 3, 2$ ).

The turnover rate of catalysis for both Ru and Fe catalysts decreases with reaction time at 293K. This decrease in rate is accompanied by loss of IR spectral features attributed to  $\text{M}(\text{CO})_3(\text{pentene})_2$  and the corresponding growth of spectral features attributed to  $\text{M}(\text{CO})_3(1,3\text{-pentadiene})$  ( $\sim 75\%$ ) and  $\text{M}(\text{CO})_4(\text{pentene})$  ( $\sim 25\%$ ) Table II, identified by comparison of IR spectra with those of authentic samples. These complexes, especially  $\text{M}(\text{CO})_3(1,3\text{-pentadiene})$ , once formed are relatively inert and show no catalytic activity. Formation of  $\text{M}(\text{CO})_4(\text{pentene})$  is reasonable, considering that catalyst decomposition would release CO which can react with  $\text{M}(\text{CO})_3(\text{pentene})_2$  to give  $\text{M}(\text{CO})_4(\text{pentene})$ . The dehydrogenation of 1-pentene to yield inert 1,3-pentadiene complexes is a new finding. The mechanism of 1-pentene

dehydrogenation deserves further study; previous work<sup>25</sup> rules out the intermediacy of 1,3,4,5-n-pent-4-ene-3,1-yliron tricarbonyl as an intermediate leading to  $\text{Fe}(\text{CO})_3(1,3\text{-pentadiene})$ . Evidence for the formation of  $\text{Ru}(\text{CO})_3(1,3\text{-pentadiene})$  comes from GC-mass spectra and HPLC analysis of the metal containing product from the catalytic mixture. The GC-mass spectra show a molecular ion peak ( $M^+=254$ ) and fragmentation pattern consistent with  $M^+-\text{CO}$ ,  $M^+-2\text{CO}$ ,  $M^+-3\text{CO}$ . This pattern is indistinguishable from that obtained from an authentic sample of  $\text{Ru}(\text{CO})_3(1,3\text{-pentadiene})$ . In addition, both GC and HPLC show the same retention time for the organometallic species recovered from the catalytic samples and an authentic sample.

d. Photochemical Formation of  $\text{HM}(\text{CO})_3(\eta^3\text{-allyl})$ . We expect the catalytic cycle for Ru to be similar to that for  $\text{Fe}(\text{CO})_5$ -photocatalyzed alkene isomerization. Beyond the involvement of the  $\text{M}(\text{CO})_3(\text{alkene})_2$  we prefer not to speculate extensively here about the particular steps of the catalytic cycle, except to note the previous observation<sup>5</sup> of  $\text{HFe}(\text{CO})_3(\eta^3\text{-allyl})$ , potentially the essential intermediate in the catalytic cycle. We find that the major product of irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$  in a 90K methylcyclohexane glass exhibits two features, one sharp feature at  $2064\text{ cm}^{-1}$  and a broader absorbance with a maximum at about  $1994\text{ cm}^{-1}$ . These features are unrelated to those for  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ ;  $\text{Fe}(\text{CO})_4$  is also a minor product which accounts completely for the remaining  $1946\text{ cm}^{-1}$  product feature previously attributed to one of three characteristic carbonyl features for  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ . Warmup of the irradiated 90K glass to 173K yields conversion to a three band pattern attributable to  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ <sup>5</sup> ( $2066$ ,  $2003$  and  $1994\text{ cm}^{-1}$ ) on the basis of spectral similarity to  $\text{BrFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ <sup>26</sup> and the structurally related 1,3,4,5,-n-pent-4-ene-3,1-yliron tricarbonyl,<sup>25</sup> Table II.

Chemical evidence for the  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  has been obtained by producing  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  in a methylcyclohexane/1-bromo-2-methylpropane matrix (~50/50 by volume) at 90K. Warming above ~200K yields IR spectral changes consistent with

regeneration of  $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$  (~80%) and formation of the known  $\text{BrFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  (~20%).<sup>26</sup> Similarly, irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$  in a 90K methylcyclohexane glass followed by addition of  $\text{CCl}_4$  and warmup to 298K yields  $\text{CHCl}_3$  and the known<sup>26</sup>  $\text{ClFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ . Metal hydrides are known to react with alkyl halides<sup>27</sup> providing evidence for the existence of  $\text{HFe}(\text{CO})_3(\eta^3\text{-allyl})$ . It should also be pointed out that metal-centered radicals can also react with alkyl halides to produce the metal halide,<sup>28</sup> and radicals, e.g.  $\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ , are known to be produced upon irradiation of  $\text{Fe}(\text{CO})_5$  in the presence of  $\text{C}_3\text{H}_6$ .<sup>6</sup> We have irradiated  $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$  through Pyrex ( $\lambda > 280$  nm) and find no IR evidence for the known<sup>29</sup>  $\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  species. Thus, we conclude the  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  to be the dominant, essential species in the catalyzed isomerization of alkenes upon irradiation of  $\text{Fe}(\text{CO})_5$  through Pyrex.

The three IR band pattern (2066, 2003, 1994  $\text{cm}^{-1}$ ) attributed to  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  at 173K is retained on cooling to 90K, but photochemical reaction occurs at 90K to give the initial two band pattern, (2064, 1994  $\text{cm}^{-1}$ ), without additional CO loss, consistent with the existence of two isomers of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ . Two isomers of  $\text{XFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  ( $\text{X} = \text{Cl, Br, I}$ ) are known<sup>30</sup> and we believe these to be related to the two isomers of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ . Preliminary results show that the thermodynamically stable isomer of  $\text{XM}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  ( $\text{X} = \text{Cl, Br; M} = \text{Fe, Ru}$ ) can photochemically converted to the less stable isomer.<sup>31</sup>

Irradiation of the two band isomer of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  at 90K in a  $\text{C}_3\text{H}_6$ -containing alkane glass yields loss of additional CO and growth of a single CO-stretching feature at 1929  $\text{cm}^{-1}$ , too low in energy to be attributable to an  $\text{Fe}(\text{CO})(\text{alkene})_4$  species analogous to  $\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)_4$ . The product responsible for the 1929  $\text{cm}^{-1}$  feature was previously misidentified as trans- $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$ . Our

data clearly indicate that there are between two and three photoejected CO's (2132  $\text{cm}^{-1}$ ) for each  $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$  molecule consumed.<sup>32</sup> Near-UV irradiation of  $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$  (formed *in situ* via photolysis of  $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$  plus  $\text{C}_3\text{H}_6$  at 210K) at 100K in the presence of a large excess of  $\text{C}_3\text{H}_6$ , Figure 10, yields free CO (2132  $\text{cm}^{-1}$ ), the two band isomer of  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ , and a strong feature at 1929  $\text{cm}^{-1}$ . The amount of photogenerated CO<sup>32</sup> is consistent with loss of two CO's per molecule of  $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$  converted to the 1929  $\text{cm}^{-1}$  product based on quantitation of consumed  $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$  [ $\nu$ ,  $\text{cm}^{-1}(\epsilon, \text{M}^{-1}\text{cm}^{-1}) = 2052 (1,200 \pm 100)$ ; 3-methylpentane, 90K] and photogenerated  $\text{HFe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$  [ $\nu$ ,  $\text{cm}^{-1}(\epsilon, \text{M}^{-1}\text{cm}^{-1}) = 2065 (7,200 \pm 700)$ ; 3-methylpentane, 90K] by FTIR. The cis- $\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_6)_3$  complex is never observed as a photoproduct from irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$  or  $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$  in the presence of excess  $\text{C}_3\text{H}_6$ . In the presence of only small amounts of  $\text{C}_3\text{H}_6$ , the 1929  $\text{cm}^{-1}$  feature grows in only very weakly, suggesting that consumption of  $\text{C}_3\text{H}_6$  by the (unobserved) product of CO loss from  $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$  leads to formation of the 1929  $\text{cm}^{-1}$  product. When samples containing the 1929  $\text{cm}^{-1}$  absorber are warmed to ~150K, the 1929  $\text{cm}^{-1}$  feature disappears and  $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$  is formed with associated consumption of free CO. Interestingly, spectral changes similar to those accompanying irradiation of  $\text{Fe}(\text{CO})_4(\text{1-pentene})$  in a neat 1-pentene glass, while cis- $\text{Fe}(\text{CO})_2(3,3\text{-dimethyl-1-pentene})_3$  is the final product of near-UV irradiation of  $\text{Fe}(\text{CO})_4(3,3\text{-dimethyl-1-pentene})$  in a 3-methylpentane glass containing 2 M 3,3-dimethyl-1-pentene at 90K. These results suggest that the low energy feature at ~1929  $\text{cm}^{-1}$  obtains only for alkenes containing allylic hydrogens, for which cis- $\text{Fe}(\text{CO})_2(\text{alkene})_3$  complexes are not accumulated as photoproducts. The 90K irradiation of  $\text{Fe}(\text{CO})_{5-n}(^{13}\text{CO})_n$  (~20% <sup>13</sup>C) in a  $\text{C}_3\text{H}_6$ -saturated 3-methylpentane glass yields final product features at 1929 and 1885  $\text{cm}^{-1}$  consistent with formulation of the 1929  $\text{cm}^{-1}$  absorber as monocarbonyl or a trans-dicarbonyl species exhibiting an interaction force constant  $K_f = 0$ . The two dicarbonyl complexes cis-

and trans-Fe(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> exhibit significant interaction force constants and it is therefore unlikely that an Fe(CO)<sub>2</sub>(C<sub>3</sub>H<sub>6</sub>)<sub>n</sub> complex would have  $K_f = 0$ . On the basis of the evidence available, we tentatively formulate the 1929 cm<sup>-1</sup> absorber as HFe(CO)(C<sub>3</sub>H<sub>6</sub>)<sub>2</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>). We do not find evidence for formation of ( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>Fe(CO)<sub>2</sub>.<sup>33</sup>

Complete conversion of Ru<sub>3</sub>(CO)<sub>12</sub> to Ru(CO)<sub>4</sub>(1-pentene) can only be done in the presence of a large excess of 1-pentene ( $>1$  M). Photolysis of Ru(CO)<sub>4</sub>(1-pentene) in either methylcyclohexane or 3-methylpentane glasses containing 1.0 M 1-pentene at 90K results in photoejection of CO (2132 cm<sup>-1</sup>) and formation of mostly Ru(CO)<sub>3</sub>(1-pentene)<sub>2</sub>. The generation of Ru(CO)<sub>3</sub>(1-pentene)<sub>2</sub> is probably due to reaction of 1-pentene present in the glass with the 16-electron Ru(CO)<sub>3</sub>(1-pentene) fragment (not observed). When a 3-methylpentane matrix containing Ru(CO)<sub>4</sub>(1-pentene) is photolyzed at 55K, IR spectral changes for the photolysis reveal the generation of free CO (2132 cm<sup>-1</sup>) and growth of new spectral features which are different from those observed with alkene = C<sub>2</sub>H<sub>4</sub>. These new features are attributed to HRu(CO)<sub>3</sub>( $\eta^3$ -C<sub>5</sub>H<sub>9</sub>) on the basis of spectral similarity to the IR bands of HFe(CO)<sub>3</sub>( $\eta^3$ -C<sub>5</sub>H<sub>9</sub>). The ability to detect the HRu(CO)<sub>3</sub>( $\eta^3$ -C<sub>5</sub>H<sub>9</sub>) at the lower temperature reflects slower 1-pentene diffusion and/or a slower rate of 1-pentene binding to the unsaturated Ru center. Due to the experimental difficulty, the trapping reaction of HRu(CO)<sub>3</sub>( $\eta^3$ -C<sub>5</sub>H<sub>9</sub>) with alkyl halides has not yet been successful.

Conversion of Ru<sub>3</sub>(CO)<sub>12</sub> to Ru(CO)<sub>4</sub>(C<sub>3</sub>H<sub>6</sub>) is not complete, even after prolonged irradiation in solution saturated with C<sub>3</sub>H<sub>6</sub>. Presumably, a photostationary state is reached, and upon switching off the light source, we observe reformation of Ru<sub>3</sub>(CO)<sub>12</sub>. However, HRu(CO)<sub>3</sub>( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) can still be generated as a minor product (<10%) at 90K by photolysis of Ru(CO)<sub>4</sub>(C<sub>3</sub>H<sub>6</sub>) in the presence of Ru<sub>3</sub>(CO)<sub>12</sub> in a C<sub>3</sub>H<sub>6</sub>-containing methylcyclohexane glass. The other products are Ru<sub>3</sub>(CO)<sub>11</sub>(C<sub>3</sub>H<sub>6</sub>) and Ru(CO)<sub>3</sub>(C<sub>3</sub>H<sub>6</sub>)<sub>2</sub>.

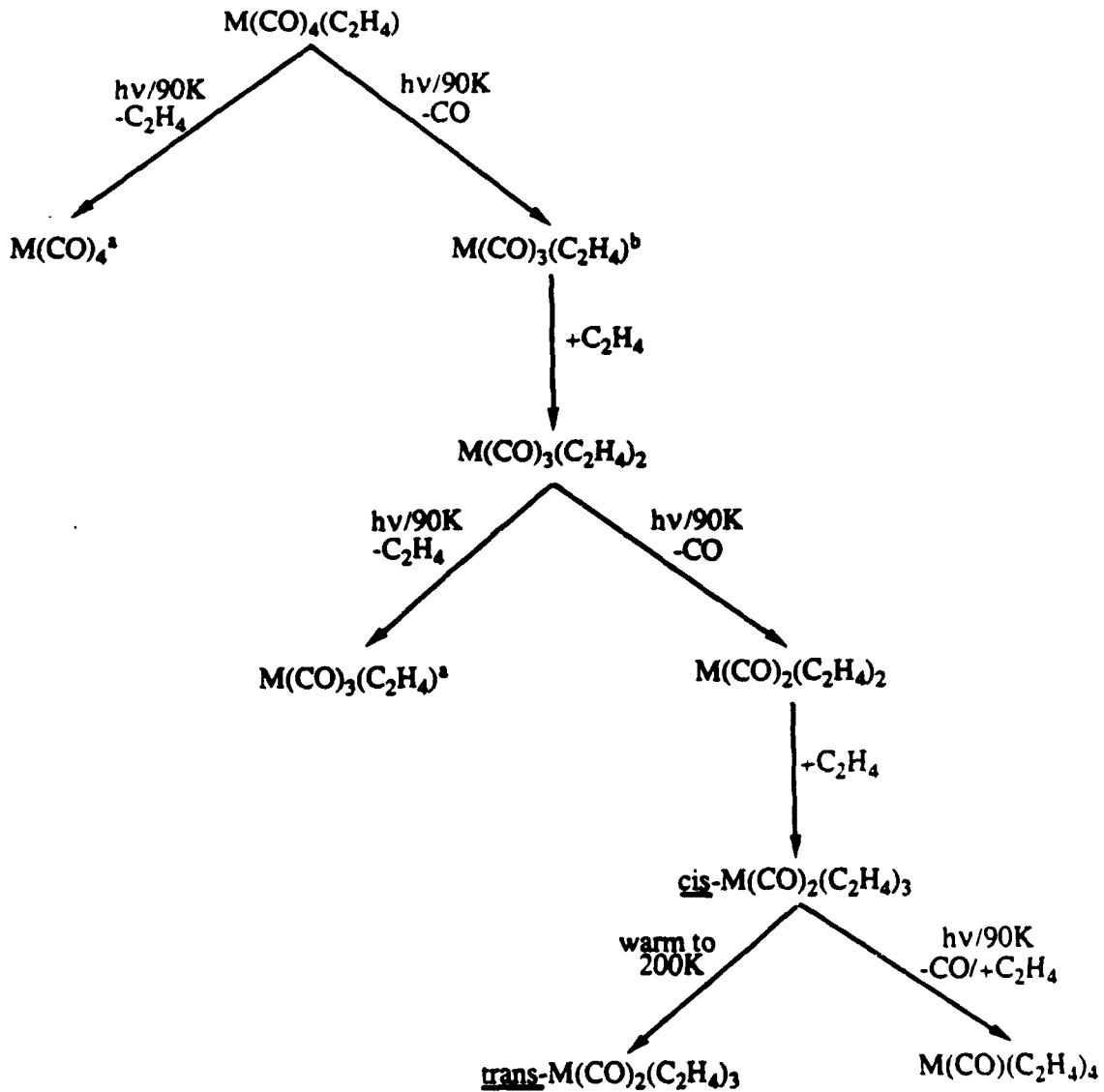
### Conclusions

Scheme I summarizes the photochemistry of  $M(CO)_n(C_2H_4)_{5-n}$  ( $M = Fe, Ru$ ;  $n = 4, 3, 2$ ) Interestingly, warmup of glasses containing  $M(CO)(C_2H_4)_4$  leads to nearly quantitative regeneration at 298 K of  $M(CO)_4(C_2H_4)$  ( $M = Ru$ ) or a mixture of  $M(CO)_4(C_2H_4)$  and  $M(CO)_3(C_2H_4)_2$  ( $M = Fe$ ). Thus, the photochemical substitution of CO by  $C_2H_4$  is reversible. The  $M(CO)_2(C_2H_4)_3$  and  $M(CO)_3(C_2H_4)_2$  complexes serve as catalyst precursors for the isomerization of 1-pentene, consistent with the conclusion that  $\pi$ -allyl hydride species are essential in the catalytic cycle. The photochemistry of the  $Fe(CO)_n(C_3H_6)_{5-n}$  complexes, Scheme II, shows that  $\pi$ -allyl-hydride species can actually be detected. The  $\pi$ -allyl-hydride reacts thermally with alkyl halides, providing additional chemical evidence for its formulation.

The data for the  $M(CO)_3(alkene)_2$  complexes support the conclusion that, in general, the loss of CO or alkene can be expected from complexes containing both CO and alkene. This finding is consistent with the fact that CO and alkene are both  $\pi$ -acceptor ligands. The relative importance of CO vs. alkene loss has not been determined, but since we now know the various product identities, we are in a position to make a systematic investigation for the Fe and Ru complexes as has been done with  $W(CO)_5(alkene)$ .<sup>32</sup> Our finding that alkene can be dissociated photochemically is consistent with work on  $Fe(CO)_3(\pi^4-1,3\text{-butadiene})$  which forms  $Fe(CO)_2(\pi^4-1,3\text{-butadiene})$  and  $Fe(CO)_3(\pi^2-1,3\text{-butadiene})$  upon photoexcitation in rigid media at low temperature.<sup>23</sup>

The photogenerated  $M(CO)_3(alkene)_2$  and  $M(CO)_2(alkene)_3$  complexes provide useful entries to derivatives of  $M(CO)_5$  because the alkenes are so labile. Such reactive complexes may be useful in preparing substitution derivatives which are thermally or photochemically sensitive. In terms of understanding photocatalyzed reactions of alkenes, the characterization of the photoreactions of  $M(CO)_n(alkene)_{5-n}$  is an important step in providing a step-by-step rationale of the

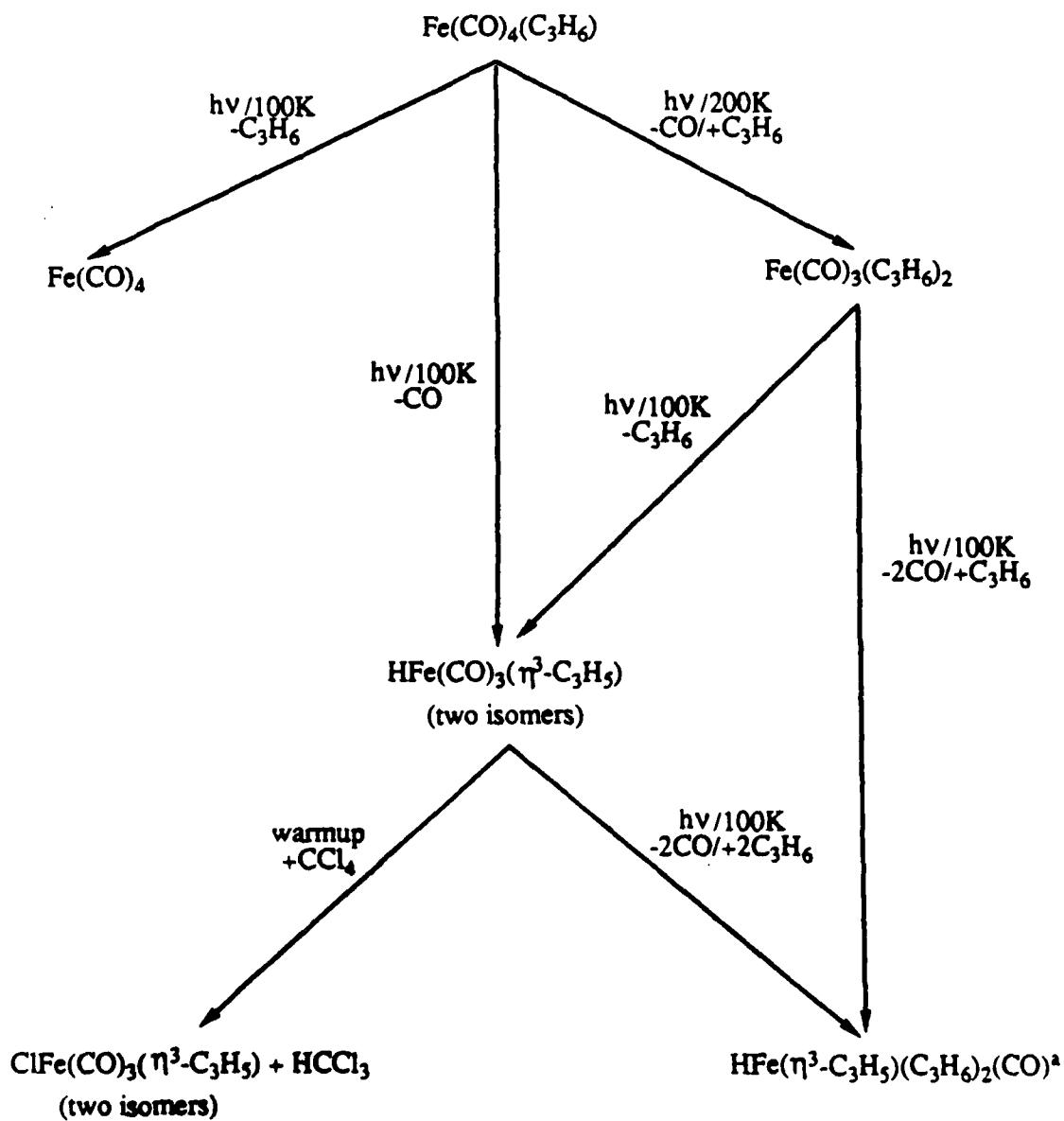
**Scheme I.** Summary of the photochemistry of  $M(CO)_n(C_2H_4)_{5-n}$  ( $M = Fe, Ru$ ;  $n = 4, 3, 2$ ).



<sup>a</sup>Not detected for  $M = Ru$

<sup>b</sup>Detection requires  $T < 90K$  for  $M = Ru$

Scheme II. Summary of the photochemistry of  $\text{Fe}(\text{CO})_n(\text{C}_3\text{H}_6)_{5-n}$  ( $n = 4, 3$ ).



\*Identification of this compound is tentative.

catalytic chemistry. Further, the eventual finding of  $M(CO)_3(1,3\text{-pentadiene})$  in ~75% yield (~25%  $M(CO)_4(\text{pentene})$ ) from thermal reaction of  $M(CO)_3(C_2H_4)_2$  with 1-pentene provides a rationale for finite turnover number from a system that appears to be so reversible when considering only the  $C_2H_4$  complexes. Further work is needed to establish the mechanism of the dehydrogenation of 1-pentene, but the consequence is clear: the 1,3 pentadiene effectively suppresses catalytic action by leading to formation of  $M(CO)_3(1,3\text{-pentadiene})$ .

One final point should be made concerning intermediates formed from  $M(CO)_n(\text{alkene})_{5-n}$  ( $n = 4, 3, 2$ ). We find no evidence for high concentrations of radical species, consistent with the levels of such species previously suggested.<sup>6</sup> However, it is well-appreciated that very active species, though present in small concentration, can be catalytically significant. While it is known that  $Fe(CO)_3(\eta^3\text{-C}_3H_5)$  radicals are very active catalysts for alkene isomerization,<sup>34</sup> it appears that the  $M(CO)_3(\text{alkene})_2$  and  $M(CO)_2(\text{alkene})_3$  can account for the photocatalytic activity of  $Fe(CO)_5$  or  $M_3(CO)_{12}$ .

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Table I. UV-Visible Data for Relevant Compounds.

Species	Medium (T,K)	$\lambda$ , nm ( $\epsilon$ )
$\text{Ru}_3(\text{CO})_{12}$	MCH(298)	237(30,200), 278(sh), 325(sh) 391(7200)
$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$	MCH(298)	240(3400), 266(1700)
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	MCH(298)	220(11,700), 262(4900)
$\text{Ru}(\text{CO})_3(1,3\text{-pentadiene})$	MCH(298)	245 (10,000), 280(7600)
$\text{Fe}(\text{CO})_5$	3MP(90)	242(21,000), 290(5200)
$\text{Fe}(\text{CO})_4$	3MP(90)	390
$\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$	MCH(298)	255(sh, ~10,000)
$\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$	MCH(298)	234, 447
$\text{Fe}(\text{CO})_4(\text{C}_3\text{H}_6)$	MCH(298)	255(sh, ~10,000)

<sup>a</sup> MCH  $\equiv$  methylcyclohexane; 3MP  $\equiv$  3-methylpentane.

Table II. IR Data for Relevant Complexes.

Species	Medium (T, K) <sup>a</sup>	$\nu$ , $\text{cm}^{-1}$ ( $\epsilon$ or Rel. Abs.)
$\text{Ru}_3(\text{CO})_{12}$	3MP (298)	2061(24,500); 2031(14,600); 2012(9000)
$\text{Ru}(\text{CO})_5$	3MP (298)	2037(1.0); 2002(1.4)
$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$	3MP (298) 3MP (90)	2104(470); 2023(8100); 1996(4000) 2106(980); 2023(9900); 1994(8000)
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)$	3MP (55)	2055(1.0); 1978(1.2); 1972(1.3)
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	3MP (298) 3MP (90)	2081(320); 2005(2100); 1995(6500) 2082(350); 2004(1300); 1993(7200)
<u>trans</u> - $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$	3MP (233) 3MP (90)	1956 1953
<u>cis</u> - $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$	MCH (90)	2019(1.4); 1975(1.0)
$\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$	MCH (90)	2020(1.0); 1948(1.3)
$\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_4$	MCH (90)	1964
$\text{Ru}(\text{CO})(\text{C}_2\text{H}_4)_3^b$	MCH (90)	1923
$\text{Ru}(\text{CO})_4(\text{C}_3\text{H}_6)$	3MP (298) MCH (90)	2100(1.0); 2018(10.6); 1991(6.4) 2101(1.0); 2018(11.5); 1987(6.4)
HRu(CO) <sub>3</sub> ( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) isomer(a)	MCH (90)	2082(1.0); 2008(1.2)
<u>endo</u> -BrRu(CO) <sub>3</sub> ( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )	3MP (298)	2109(1.0); 2060(1.4); 2019(1.3)
<u>exo</u> -BrRu(CO) <sub>3</sub> ( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )	3MP (298)	2107(1.0); 2055(1.1); 2025(1.2)
$\text{Ru}(\text{CO})_3(\text{C}_3\text{H}_6)_2$	3MP (298)	2075(1.0); 2005(3.3); 1988(14)
<u>trans</u> - $\text{Ru}(\text{CO})_2(\text{C}_3\text{H}_6)_3$	3MP (233)	1949
$\text{Ru}(\text{CO})_4(1\text{-pentene})$	3MP (298) 3MP (90) 3MP (55) 1-pentene (90)	2100(1.9); 2018(9.3); 1989(5.8) 2102(1.0); 2019(8.9); 1988(6.0) 2102(1.0); 2019(8.5); 1987(5.5) 2102 (1.0); 2020(10.1); 1983(7.0)
HRu(CO) <sub>3</sub> ( $\eta^3$ -C <sub>5</sub> H <sub>9</sub> )	MCH (90) 3MP (55)	2078(1.0); 2004(1.2) 2078(1.0); 2003(1.2)
$\text{Ru}(\text{CO})_3(1\text{-pentene})_2$	3MP (298) 3MP (90) 1-pentene (90)	2072(1.0); 2000(2.6); 1987(9.4) 2073(1.0); 2000(1.6); 1987(8.4) 2076(1.0); 2000(1.8); 1984(8.9)
<u>trans</u> - $\text{Ru}(\text{CO})_2(1\text{-pentene})_3$	3MP (233)	1946

Table II. (continued)

Ru(CO) <sub>4</sub> (3,3-dimethyl-1-pentene)	(CH <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>8</sub> (298)	2099(1.0); 2017(5.6); 1990(3.6)
Ru(CO) <sub>3</sub> (3,3-dimethyl-1-pentene) <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>8</sub> (233)	2077(1.0); 1995(2.3); 1986(10.0)
Ru(CO) <sub>3</sub> ( <i>trans</i> -1,3-pentadiene)	3MP (298)	2062(3600); 1997(6500); 1986(5400)
Ru(CO) <sub>4</sub> (PPh <sub>3</sub> )	3MP (298)	2061(2600); 1987(1000); 1954(4300)
Ru(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>	3MP (298)	1907(3300)
Fe(CO) <sub>5</sub>	3MP (298) 3MP (90)	2023(9600); 2001(14,000) 2023(15,000); 1996(19,000)
Fe(CO) <sub>4</sub>	MCH (90)	2083(1.0); 1988(12); 1979(4.5) 1946(14)
Fe(CO) <sub>4</sub> (C <sub>2</sub> H <sub>4</sub> )	MCH (298) MCH (90)	2087(1300); 2013(sh); 2007(10,000); 1984(6700) 2088(2200); 2011(sh); 2006(12,000); 1980(10,000)
Fe(CO) <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> )	MCH (90) Ar (10) <sup>c</sup>	2041(1.0); 1963(1.3); 1957(1.6) 2039, 1976, 1950
Fe(CO) <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	MCH (273) MCH (90) CF <sub>3</sub> C <sub>6</sub> F <sub>11</sub> (273)	2060(940); 1988(sh, ~5100); 1981(12,600) 2060(1.0); 1988(4.8); 1981(12) 2064(1.0); 1997(5.0); 1988(13.6)
<i>trans</i> -Fe(CO) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub>	MCH (90)	1942
<i>cis</i> -Fe(CO) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub>	MCH (90)	1998(1.5); 1955(1.0)
Fe(CO) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	MCH (90)	2003(1.0); 1938(1.3)
Fe(CO)(C <sub>2</sub> H <sub>4</sub> ) <sub>4</sub>	MCH (90)	1952
Fe( <sup>13</sup> CO)(C <sub>2</sub> H <sub>4</sub> ) <sub>4</sub>	MCH (90)	1908
Fe(CO) <sub>4</sub> (C <sub>3</sub> H <sub>6</sub> )	MCH (298) MCH (90)	2082(1800); 2006(sh); 2001(12,000); 1980(7500) 2083(2900); 2006(sh); 2001(15,000); 1976(12,000)
HFe(CO) <sub>3</sub> ( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) isomer(a) isomer(b)	MCH (90) MCH (173)	2064(1.0); 1994(1.5) 2066(1.0); 2003(1.5); 1994(1.2)
Fe(CO) <sub>3</sub> ( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sup>d</sup>	Pet. Ether (298)	2046, 1968, 1960
Fe(CO) <sub>3</sub> (C <sub>3</sub> H <sub>6</sub> ) <sub>2</sub>	MCH (90)	2051(1.0); 1971(11)

Table II. (continued)

HFe(CO)(C <sub>3</sub> H <sub>6</sub> ) <sub>2</sub> (η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> ) <sup>b</sup>	MCH (90)	1929
Fe(CO) <sub>4</sub> (3,3-dimethyl-1-pentene)	3MP (298)	2079(1.0); 2003(sh); 1997(4.0)
	3MP (90)	1978(3.1) 2080(1.0); 2003(1.6); 1996(3.3) 1973(2.9)
Fe(CO) <sub>3</sub> (3,3-dimethyl-1-pentene)	3MP (90)	2041(1.0); 1966(1.1); 1953(1.2)
Fe(CO) <sub>3</sub> (3,3-dimethyl-1-pentene) <sub>2</sub>	3MP (195)	2046(1.0); 1970(15)
<u>cis</u> -Fe(CO) <sub>2</sub> (3,3-dimethyl-1-pentene) <sub>3</sub>	3MP (90)	1989(~1.2); 1929(1.0)
Fe(CO) <sub>4</sub> (1-pentene) <sup>e</sup>	3MP (298)	2083(1.0); 2002(5.4); 1981(4.2)
Fe(CO)(η <sup>4</sup> -1,3-butadiene) <sub>2</sub> <sup>f</sup>	hexane (298)	1984.5
HFe(CO) <sub>3</sub> (η <sup>3</sup> -C <sub>5</sub> H <sub>9</sub> )	MCH (90)	2059(1.0); 1989(1.5)
Fe(CO) <sub>3</sub> (1-pentene) <sub>2</sub>	1-pentene (195)	2048(1.0); 1972(16.6)
HFe(CO)(C <sub>5</sub> H <sub>10</sub> ) <sub>2</sub> (η <sup>3</sup> -C <sub>5</sub> H <sub>9</sub> ) <sup>b</sup>	1-pentene (90)	1925
Fe(CO) <sub>3</sub> ( <u>trans</u> -1,3-pentadiene)	MCH (298)	2049(1.0); 1982(1.6); 1973(1.1)
BrFe(CO) <sub>3</sub> (η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )	MCH (298)	2089(1.1); 2043(1.4); 2010(1.0)
Fe(CO) <sub>3</sub> (η <sup>4</sup> -C <sub>5</sub> H <sub>8</sub> ) <sup>g</sup>		2053, 1994, 1989
Fe(CO) <sub>4</sub> PPh <sub>3</sub>	MCH (298)	2052(4200); 1979(3000); 1946(11,000)
Fe(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>	MCH (298)	1895(10,500)
Fe(CO) <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> )(PPh <sub>3</sub> )	MCH (298)	2022(1.0); 1961(~1.0); 1931(1.0)

<sup>a</sup> 3MP = 3-methylpentane, MCH = methycyclohexane.

<sup>b</sup> Tentative assignment; see text.

<sup>c</sup> Band positions obtained from Ref. 23.

<sup>d</sup> Band positions obtained from ref. 29.

<sup>e</sup> Contaminated with Fe(CO)<sub>5</sub>.

<sup>f</sup> Band position obtained from Ref. 20.

<sup>g</sup> Band positions for 1,3,4,5-n-pent-4-ene-3,1-ylirontricarbonyl obtained from Ref. 25.

Table III.  $^1\text{H-NMR}$  Data for  $\text{C}_2\text{H}_4$  Complexes.<sup>a</sup>

Species	Temp, K	PPM vs. $\text{SiMe}_4$
$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$	243	2.10
$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	243	2.50
$\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$	243	3.02
$\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$	273	2.37
$\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$	273	2.68
$\text{C}_2\text{H}_4$	243	5.28
$\text{C}_7\text{H}_{14}$	243	1.54

<sup>a</sup>All data are for  $\text{CF}_3\text{C}_6\text{F}_{11}$  solutions.

Table IV.  $^1\text{H-NMR}$  Peak Integration vs. Irradiation Time for  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  in  $\text{C}_2\text{H}_4$ -saturated  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution at 298K.<sup>a</sup>

Irradiation time (min)	Integration of $^1\text{H-NMR}$ Singlet			[Ru] <sup>d</sup>
	$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (2.10ppm)	$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (2.50ppm)	$\text{C}_7\text{H}_{14}^b$ (1.54ppm)	
0.0	0.64	0	1.00	1.00
0.5	0.50	0.36 (0.28) <sup>c</sup>	1.00	1.06 (1.00) <sup>e</sup>
1.0	0.37	0.63 (0.62) <sup>c</sup>	1.00	1.07 (1.01) <sup>e</sup>

<sup>a</sup> Cf. Figure 1 for actual spectra at  $t = 0$  and  $t = 1$  min.

<sup>b</sup> Used as an internal standard.

<sup>c</sup> "Predicted" integral for  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  based on consumption of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  from preceding irradiation time.

<sup>d</sup> Total (relative) Ru concentration assuming the only species present are  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  and  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ .

<sup>e</sup> Calculated using only  $t = 0.5$  and 1 min data.

Table V.  $^1\text{H-NMR}$  Peak Integration vs. Irradiation Time for  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  in  $\text{C}_2\text{H}_4$ -saturated  $\text{CF}_3\text{C}_6\text{F}_{11}$  Solution at 243K.<sup>a</sup>

Irradiation time (min)	Integration of $^1\text{H-NMR}$ Singlet				[Ru] <sup>c</sup>
	$\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$ (2.10ppm)	$\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ (2.50ppm)	$\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ (3.02ppm)	$\text{C}_7\text{H}_{14}^b$ (1.54ppm)	
0	1.46	0.09	0	1.00	1.00
0.33	1.35	0.28	0	1.00	0.99
1	1.09	0.74	0.07	1.00	0.99
2	0.91	1.06	0.15	1.00	0.99
4	0.66	1.33	0.45	1.00	0.99

<sup>a</sup> Cf. Figure 3 for actual spectra at  $t = 0$ , 0.33, and 4 min.

<sup>b</sup> Used as an internal standard.

<sup>c</sup> Total (relative) Ru concentration assuming only Ru species present are  $\text{Ru}(\text{CO})_n(\text{C}_2\text{H}_4)_{5-n}$  ( $n = 4, 3, 2$ ).

Table VI. Turnover Rates for 1-Pentene Isomerization by  $M(CO)_3(C_2H_4)_2$  ( $M = Fe, Ru$ ),  $Ru(CO)_2(C_2H_4)_3$  and Irradiated  $Ru_3(CO)_{12}$  at 293K.

Catalyst Precursor, mM	<u>M</u>	1-pentene, t, min.	% pentene			turnover rate 1-pentene/catalyst min.	
			1-	<u>trans</u> -2-	<u>cis</u> -2-		
$Fe(CO)_3(C_2H_4)_2$	5.0	4.12	0.33	76.99	16.82	6.19	568
	2.0	6.60	0.33	93.78	4.28	1.94	615
$Ru(CO)_3(C_2H_4)_2$	5.32	1.83	1	98.56	1.31	0.13	4.95
			5	96.22	3.54	0.24	2.60
			30	91.28	8.31	0.41	1.00
			120	85.07	15.16	0.77	0.43
			1440	60.37	36.17	3.46	0.09
$Ru(CO)_2(C_2H_4)_3$	2.78	1.83	1	98.13	1.20	0.07	4.37
			5	96.40	3.39	0.21	2.47
			30	90.83	8.72	0.45	1.05
			120	85.35	13.91	0.74	0.41
			1440	61.07	35.18	3.75	0.09
$Ru(CO)_2(C_2H_4)_3$	1.40	1.83	4	97.93	1.92	0.15	3.41
			20	96.62	3.21	0.17	1.11
			120	89.79	9.72	0.49	0.56
			1	98.71	1.09	0.20	8.53
			5	97.44	2.24	0.32	3.37
$Ru(CO)_2(C_2H_4)_3$	2.78	1.83	30	95.55	3.95	0.50	0.98
			60	93.98	5.43	0.59	0.66
			120	91.44	7.80	0.76	0.47
			1	98.58	1.20	0.22	9.34
			5	97.40	2.29	0.31	3.42
$Ru(CO)_2(C_2H_4)_3$	1.40	1.83	30	95.25	4.23	0.52	1.04
			60	93.65	5.74	0.61	0.70
			120	91.11	8.07	0.82	0.49
			5	98.81	1.11	0.08	3.11
			30	97.78	2.10	0.12	0.97
$Ru_3(CO)_{12}$	1.40	1.83	5	99.09	0.86	0.05	2.38
			30	98.08	1.82	0.10	0.84

Table VI. (continued)

$\text{Ru}_3(\text{CO})_{12}^{\text{a}}$	0.85	1.83	10	97.51	2.26	0.23	>5b
			20	96.10	3.46	0.31	>4b
			60	88.07	10.78	1.15	>4b
	0.85	1.83	10	97.17	2.56	0.24	>6b
			20	96.33	3.36	0.38	>4b
			60	87.91	10.92	1.17	>4b

<sup>a</sup> Conversion of  $\text{Ru}_3(\text{CO})_{12}$  to mononuclear species is complete within the first 7 minutes of continuous near-UV irradiation with a 550 W medium pressure Hg lamp.

<sup>b</sup> Turnover rate is not defined in these cases, because higher excitation rate will increase the rate of observed product formation. Thus, the numbers are lower limits, at the light intensity used,  $10^{-6}$  ein/min. The quantum yield was observed to be ~5, similar to that in ref. 11.

## Figure Captions

Figure 1.  $^1\text{H-NMR}$  spectral changes accompanying near-UV irradiation of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  in  $\text{C}_2\text{H}_4$ -saturated  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution at 298K (a) before irradiation and (b) after 1 min irradiation. Cf. Table IV for summary of integration data.

Figure 2. IR spectral changes accompanying near-UV irradiation of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  in  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane solution at 298K (a) before irradiation, (b) after 1 min irradiation, (c) difference spectrum of (a) and (b).

Figure 3.  $^1\text{H-NMR}$  spectral changes accompanying near-UV irradiation of  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  in  $\text{C}_2\text{H}_4$ -saturated  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution at 243K (a) before irradiation, (b) after 20 s irradiation, (c) after 4 min irradiation.

Figure 4. IR spectral changes accompanying near-UV irradiation of predominantly  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  [ $\nu(\text{cm}^{-1}) = 2081, 2005, 1994$ ] and some  $\text{Ru}(\text{CO})_4(\text{C}_2\text{H}_4)$  [ $\nu(\text{cm}^{-1}) = 2105, 2023, 1995$ ] in  $\text{C}_2\text{H}_4$ -saturated 3-methylpentane solution at 233K (a) before irradiation, (b) after 1 min irradiation, (c) difference spectrum of (a) and (b).

Figure 5. IR difference spectral changes accompanying near-UV irradiation of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in a  $\text{C}_2\text{H}_4$ -containing methylcyclohexane glass at 90K (a) after 5 min. irradiation, (b) after subsequent warming to 110K and recooling to 90K, (c) after subsequent warming to 210K and recooling to 90K. All difference spectra are obtained by digital subtraction of the IR spectrum for the glass prior to irradiation from spectra obtained in the subsequent designated treatments; declining spectral features in spectra a-c are associated with loss of  $\text{Ru}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in the initial 90K irradiation. Insets display the feature at  $2132\text{ cm}^{-1}$  associated with growth of free CO in the glass. The amount of CO in the glass after irradiation is unaffected by annealing to 110K. The  $2020$  and  $1948\text{ cm}^{-1}$  features are due to  $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ ; the  $2018$  and  $1975\text{ cm}^{-1}$  features are due to cis- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ , and the  $1953\text{ cm}^{-1}$  feature is due to trans- $\text{Ru}(\text{CO})_2(\text{C}_2\text{H}_4)_3$ .

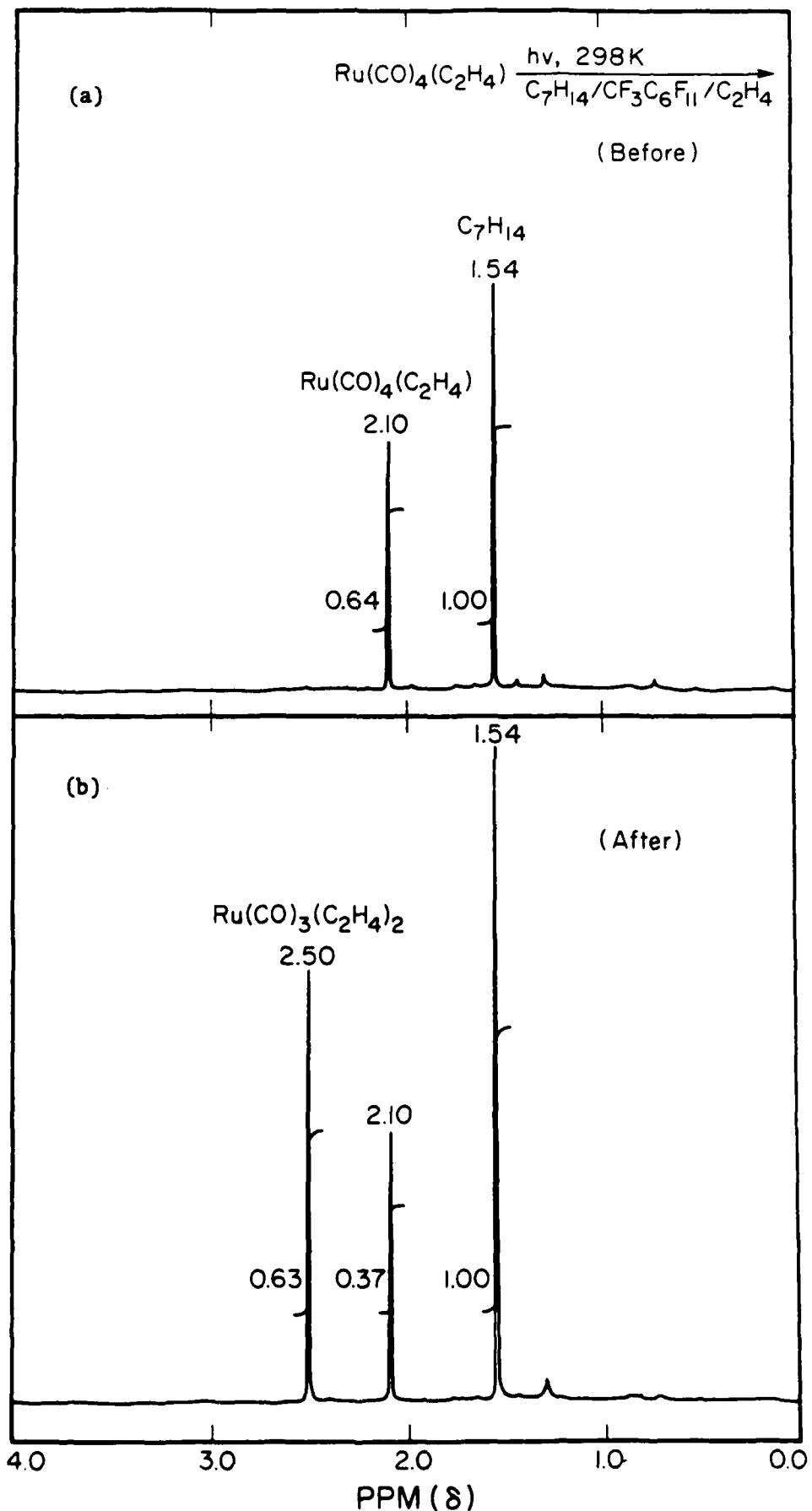
Figure 6.  $^1\text{H-NMR}$  spectral changes accompanying near-UV irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  in a  $\text{C}_2\text{H}_4$ -saturated  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution at 273K, (a) before irradiation, (b) after 30 seconds irradiation. The integrals are consistent with the photochemical conversion of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  to  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$ .

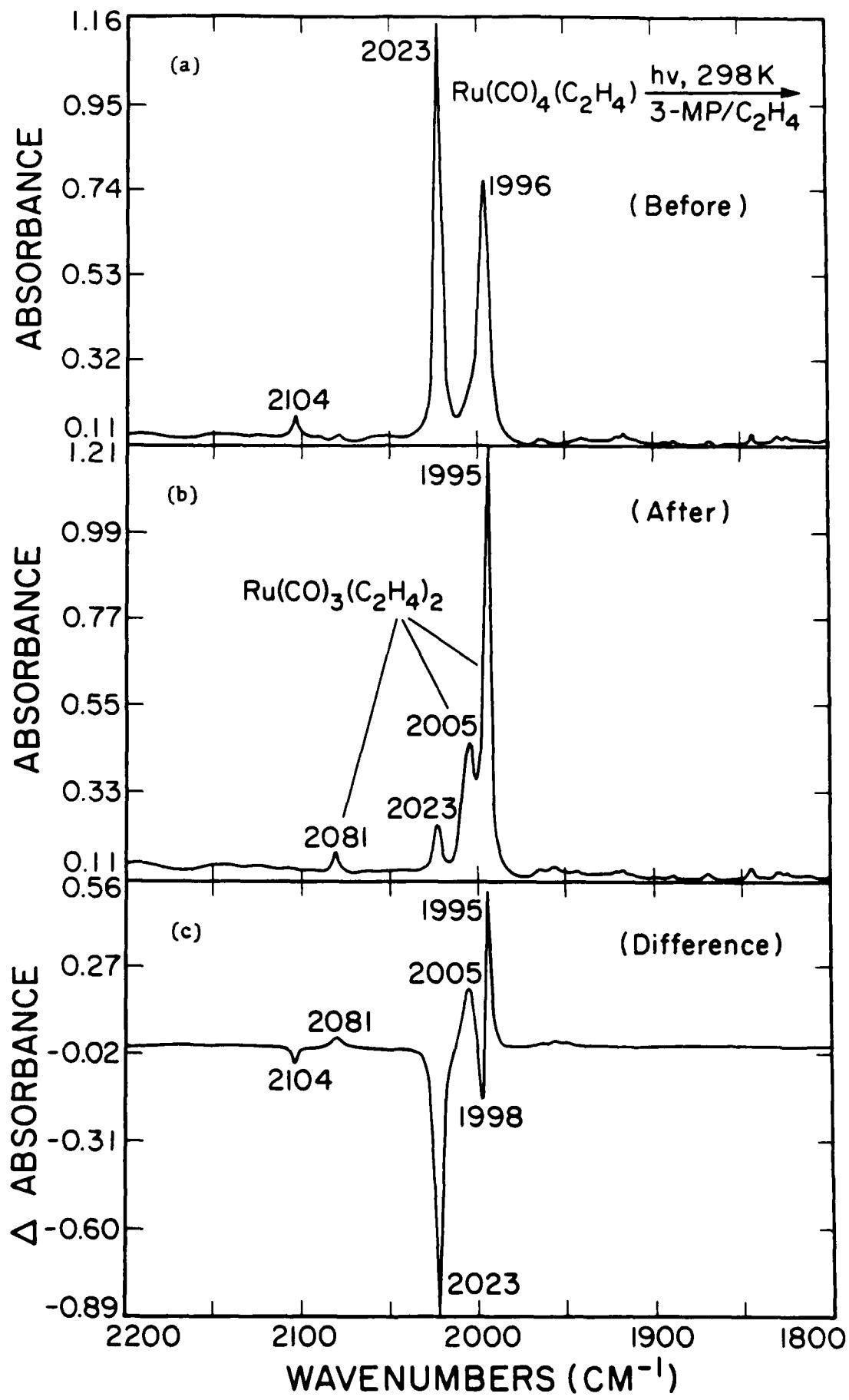
Figure 7. (a) IR difference spectrum accompanying the same near-UV irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  in  $\text{C}_2\text{H}_4$ -saturated  $\text{CF}_3\text{C}_6\text{F}_{11}$  solution at 273K for which  $^1\text{H-NMR}$  spectral changes were acquired, Figure 6; (b) IR difference spectral changes accompanying the near-UV irradiation of  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  in a  $\text{C}_2\text{H}_4$  saturated 3-methylpentane glass at 90K for 4 s and (c) 320 s.

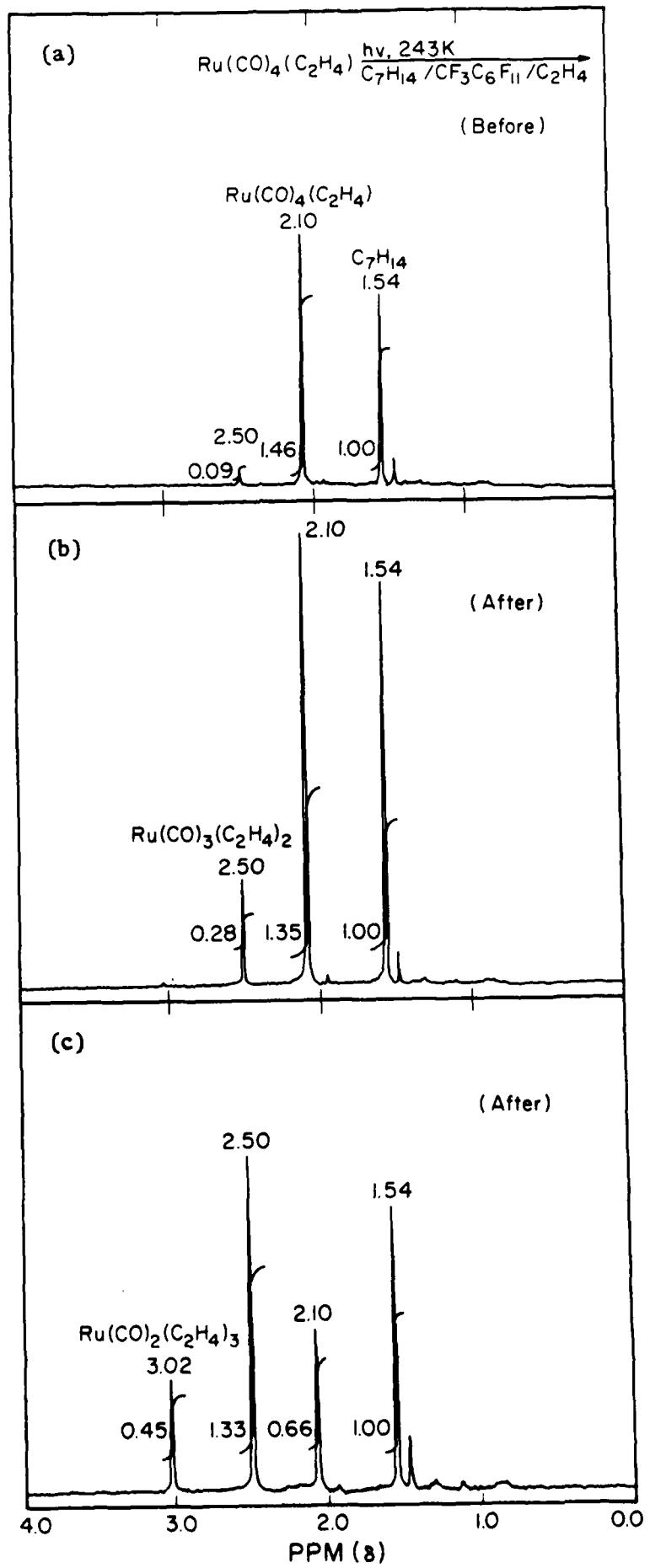
Figure 8. (a) IR difference spectrum accompanying the near-UV irradiation of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in a  $\text{C}_2\text{H}_4$ -containing 3-methylpentane glass at 100K, the  $2133\text{ cm}^{-1}$  feature is associated with the growth of free CO in the glass; (b) IR difference spectrum for the irradiated sample (spectrum a) after warming to 200K and recooling to 100K. The cis- $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_3$  [ $\nu(\text{cm}^{-1}) = 1998, 1955$ , (a)] has isomerized to the trans-isomer [ $\nu(\text{cm}^{-1}) = 1942$  (b)], and some  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  [ $\nu(\text{cm}^{-1}) = 2060, 1981$ ] has been regenerated (based on change in negative absorbances).

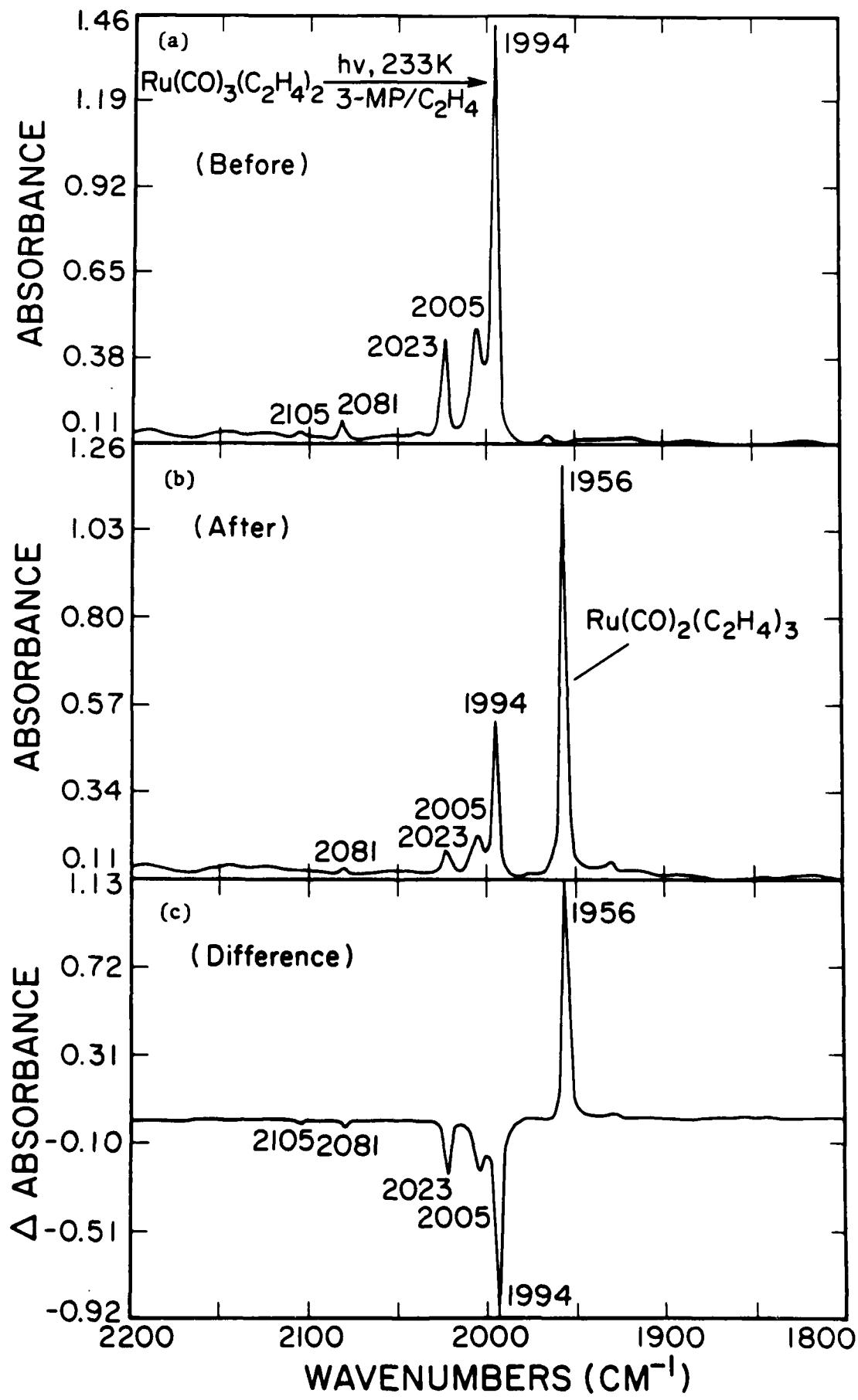
Figure 9. IR difference spectral changes accompanying near-UV irradiation of  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)_2$  in a methylcyclohexane glass at 100K. The  $2132\text{ cm}^{-1}$  feature is associated with growth of free CO; the  $2041, 1963$  and  $1957\text{ cm}^{-1}$  features are attributed to  $\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_4)$ ; the  $2003$  and  $1938\text{ cm}^{-1}$  features are attributed to  $\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_4)_2$  (see text).

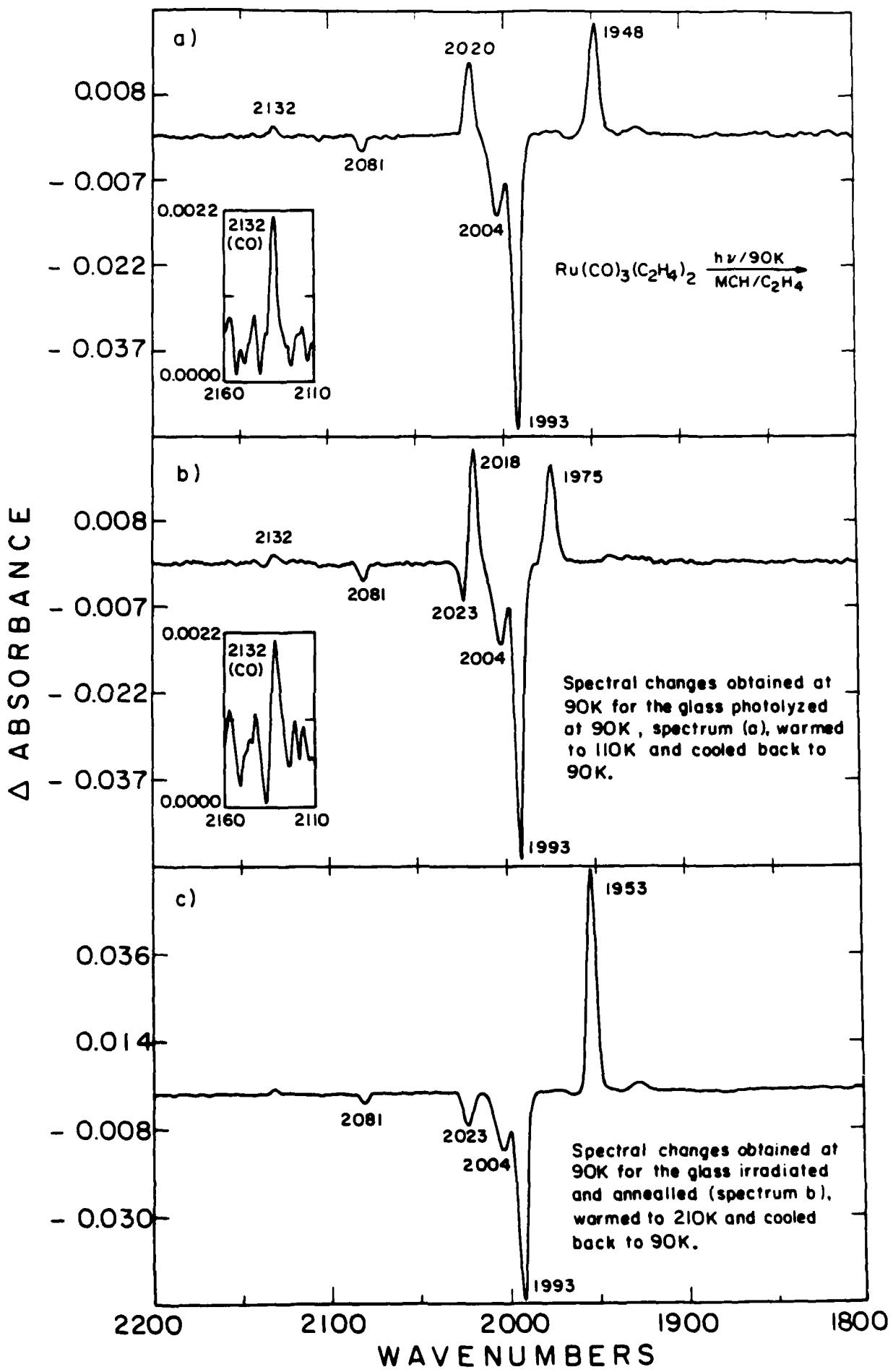
Figure 10. Infrared difference spectral changes accompanying near-UV irradiation of  $\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6)_2$  in a  $\text{C}_3\text{H}_6$ -containing methylcyclohexane glass at 100K. The  $2132\text{ cm}^{-1}$  feature is associated with growth of free CO. The features at  $2064, 1994\text{ cm}^{-1}$  are due to  $\text{HFe}(\text{CO})_3(\eta^3-\text{C}_3\text{H}_5)$ , and the  $1929\text{ cm}^{-1}$  feature is tentatively assigned as  $\text{HFe}(\text{CO})(\text{C}_3\text{H}_6)_2(\eta^3-\text{C}_3\text{H}_5)$ .

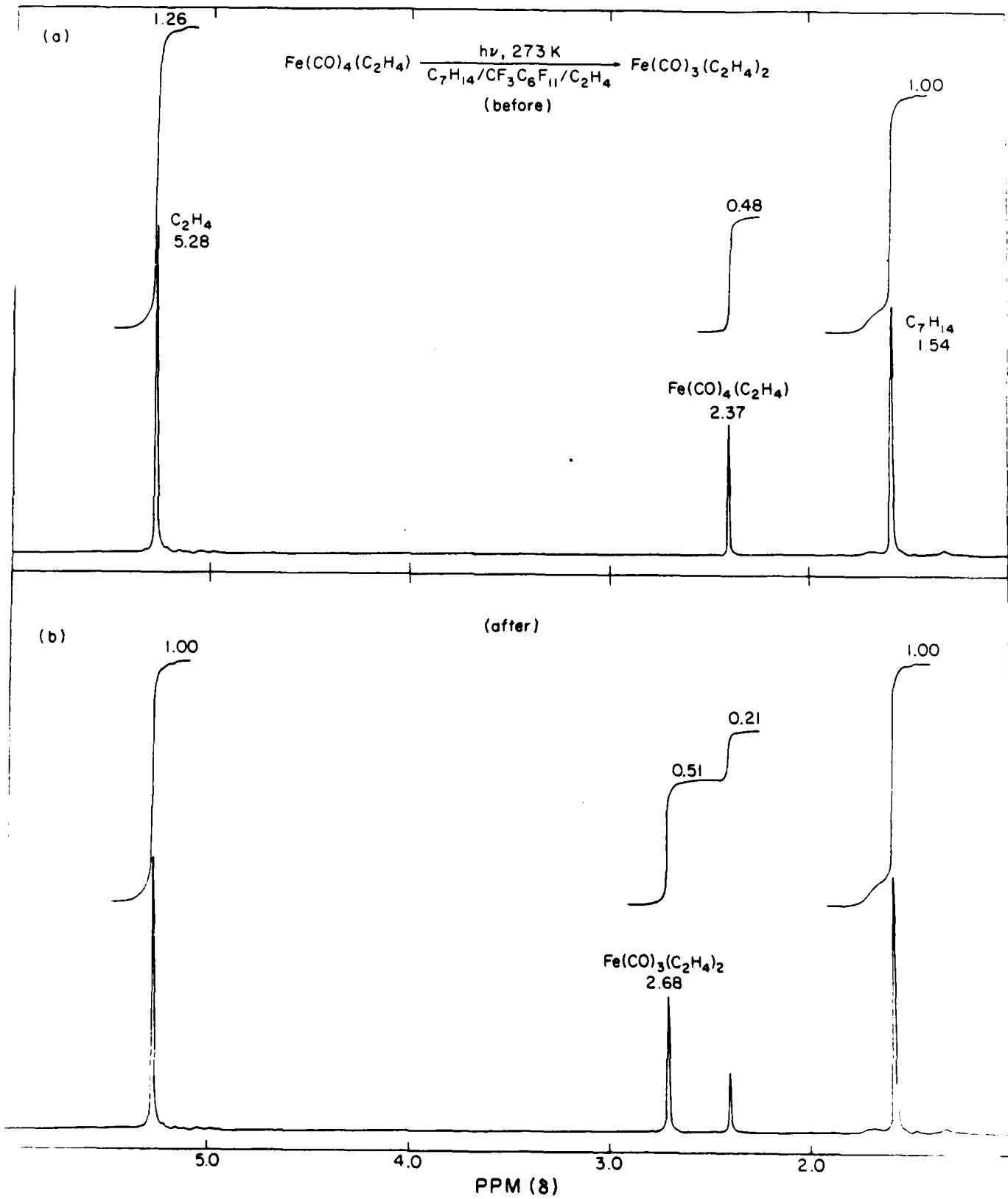


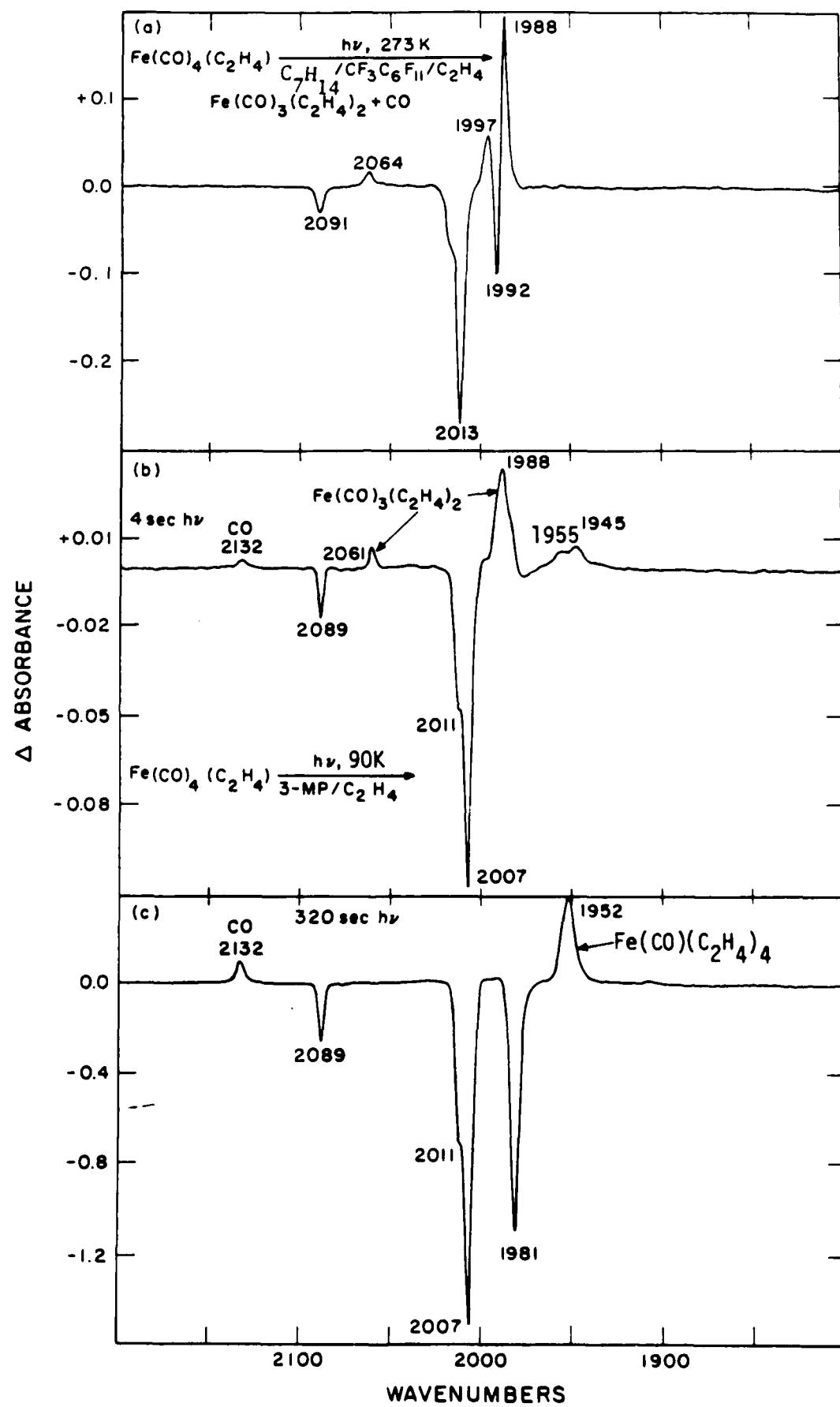


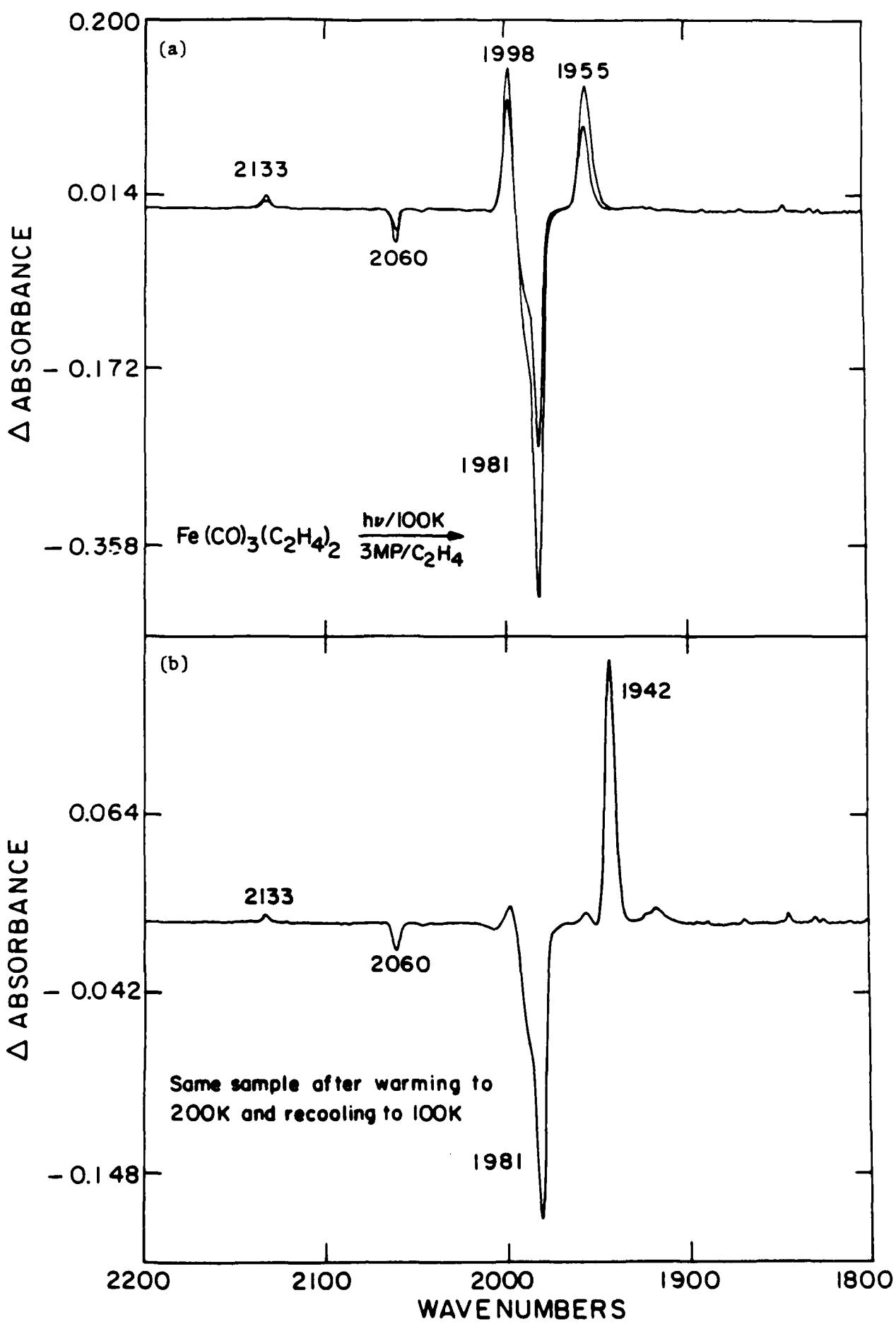


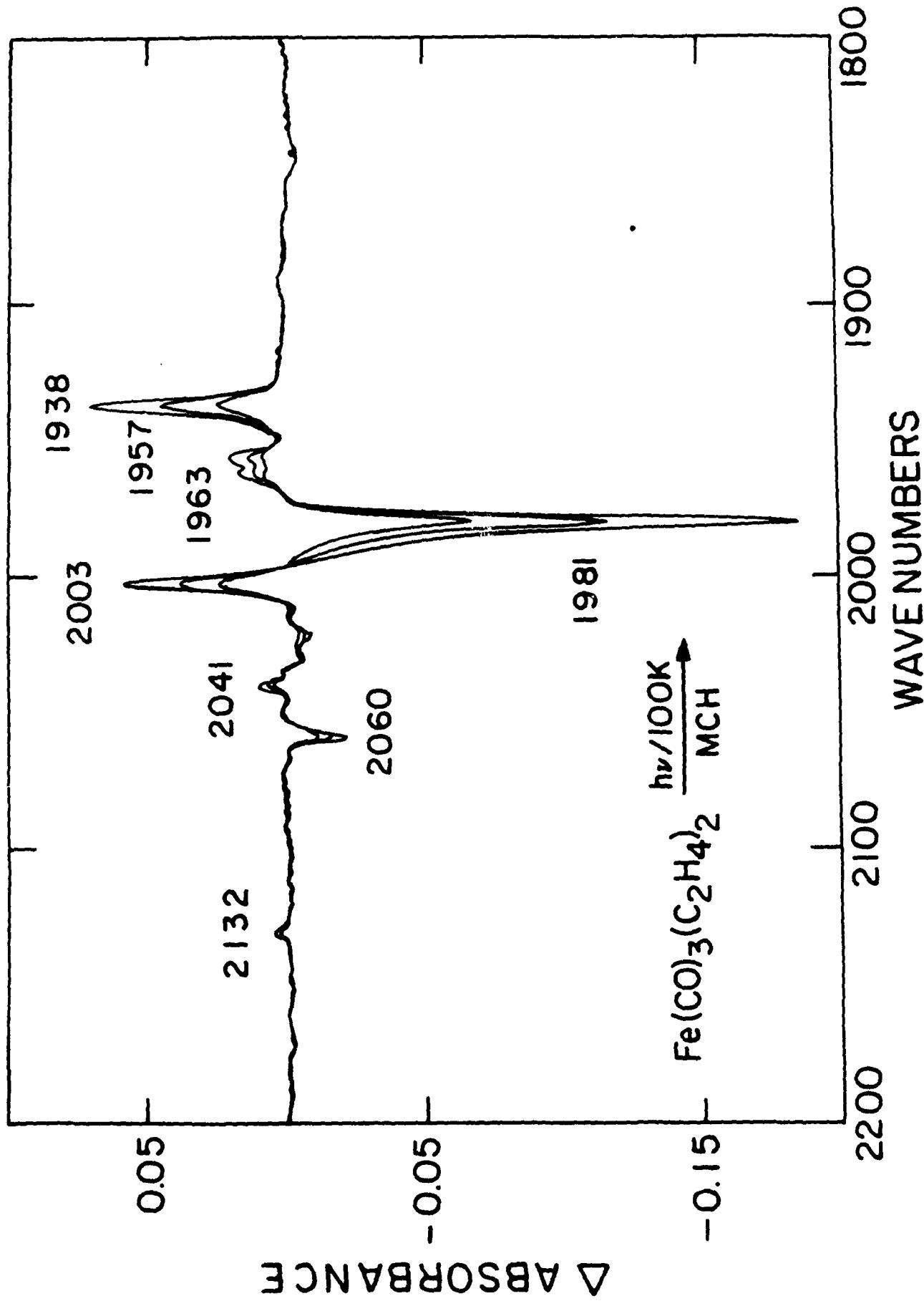


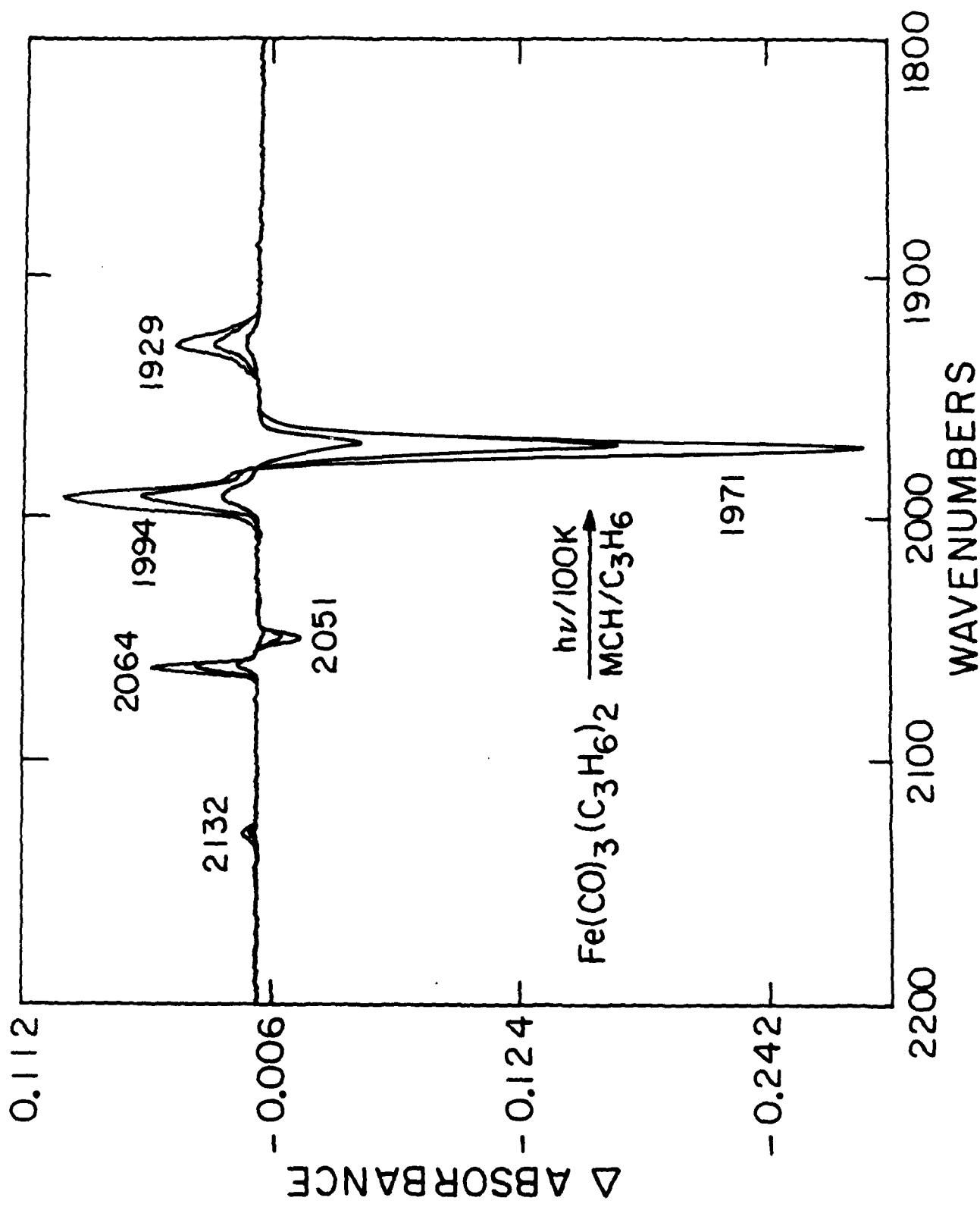












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